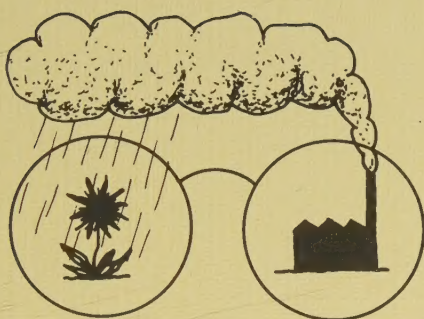




OUTDOOR ENVIRONMENTAL STUDIES USING PARTICLE INDUCED X-RAY EMISSION ANALYSIS

sampling, multivariate statistical
evaluation and instrumental development

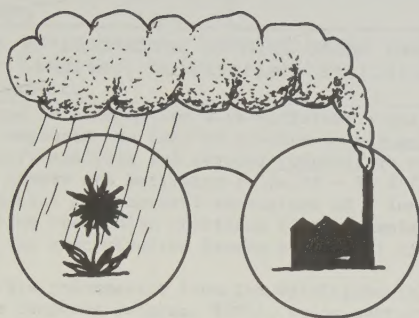
HANS-CHRISTEN HANSSON

Lund 1983



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sampling, multivariate statistical
evaluation and instrumental development

HANS-CHRISTEN HANSSON



OUTDOOR ENVIRONMENTAL STUDIES
FORMING PARTICLE INDICED
X-RAY EMISSION ANALYSIS



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Organization LUND UNIVERSITY Department of Nuclear Physics Sölvegatan 14 S - 223 62 Lund, Sweden	Document name DOCTORAL DISSERTATION Date of issue October 28, 1983 CODEN: LUTFD2/(TFKF-1007)/1-90/(1983)	
Author(s) Hans-Christen Hansson	Sponsoring organization	
Title and subtitle OUTDOOR ENVIRONMENTAL STUDIES USING PARTICLE INDUCED X-RAY EMISSION ANALYSIS - sampling, multivariate statistical evaluation and instrumental development.		
The PIXE-analysis technique in combination with different samplers was employed in rural environments. Particular emphasis was laid of studies on <u>aerosol long range transport</u>. Based on <u>air mass trajectory analysis</u> and <u>aerosol composition</u> measurements the foreign contribution in southern Sweden was estimated to be 70 - 80 % for S and Pb but only 30 - 50 % for V and Ni. The spatial and temporal extensions of a long range transport episode were studied using high time resolution continous filter samplers in a network in southern Sweden. The variation in the concentration levels of <u>sulphur</u> agreed well with changes in the air mass history. To extract the most possible information from the multielemental data base <u>multivariate statistical techniques</u>, a computer program, SIMCA, using <u>pattern recognition</u> combined with <u>principal component analysis</u>, were used. It was found that transport episodes from central Europe had a low variability in the fine mode elemental composition compared with the northerly air masses, but the elemental composition for different size fractions was clearly separated. The element composition in the different <u>size fractions</u> indicate that the <u>transformation</u> processes are more important than the original source. To be able to measure the wet deposition of different elements, especially the heavy metals, a <u>preconcentration method</u> for PIXE analysis of <u>rain water</u> has been developed. The detection limits of 0.06 - 3 µg/l, make it possible to follow about 25 different elemental concentrations simultaneously in typical Swedish rain water. A microcomputer-controlled <u>two size fractionating aerosol sampler</u> with a large sample capacity especially designed for the PIXE method was developed to facilitate sampling at optimized conditions for the sampling and analytical system. Through being able to change the particle size cut off characteristics as well as the flow rate, the sampler can be adjusted to suit most sampling requirments with the best possible elemental detection limits. The aerodynamic properties of the sampler have been tested and show losses of between 5 and 15 % in the particle size range 0.05 to 10 µm diameter.		
Key words		
Classification system and/or index terms (if any)		
Supplementary bibliographical information	Language English	
ISSN and key title	ISBN	
Recipient's notes	Number of pages	Price
	Security classification	

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Date October 28, 1983

OUTDOOR ENVIRONMENTAL STUDIES USING PARTICLE INDUCED X-RAY EMISSION ANALYSIS.

Sampling, multivariate statistical evaluation and instrumental development.

by Hans-Christen Hansson

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SUMMARY

Introduction

Man has always taken access to clear air and water for granted. The resources of air and water have been considered as infinite. However, during the last years signs of pollution far away from the pollution sources have become more and more noticeable. Even when the immediate environment was heavily polluted, it was not always considered a threat to people's health. As late as during the early 1950's, when very severe local air pollution problems (e.g. in London) claimed several lives, some unknown disease was believed to be the cause of sickness and death.

Since then much has been done to deal with local pollution problems. The aim has mainly been to avoid high levels of pollution in the area around the source. In densely populated areas the steps taken have usually consisted of releasing the polluting agents from tall chimneys in the hope that they will be removed from the area. Unfortunately the solution to the problem of pollution often seems to be regarded as just a question of dilution. In the early 60's the first signs of acidification were discovered in Sweden as well as high soot concentrations in air masses originating from the large industrialized areas in Europe.

Today the occurrence of acid rain and the long-range transport of pollutants are well known and established facts. Nevertheless we still need to gain much more knowledge, especially about transport, transformation and deposition of airborne pollution and how different ecological systems react on different pollutants, to understand what damage has been done and is being done to nature.

The existence of long-range transport implies that instead of rather small areas, large parts of the earth are affected by anthropogenic pollution. Soot from different kinds of industrial processes is found everywhere today in the northern hemisphere. The effects of the release of sulphur from burning fossil fuels are seen as acid rain causing the acidification of lakes and the dying of forests in large parts of Europe.

Acidification, which is an obvious result of pollution, has been widely observed and counteraction is being taken internationally to reduce the release of sulphur dioxide. It is, however, not known if these steps will be sufficient and how other increasing pollutants are affecting the acidification process. The pollution problems of today has grown from a local to a global problem. Thus the

problems have become more complicated and serious and also much more difficult to handle since they are now international.

Many alarming reports about severe and sometimes irreparable damage due to modern man's negligent treatment of nature have been made during the last years. The coming of catastrophes has even been forecast. Despite the fact that that there are strong arguments against such catastrophes, scientists are today far from certain about the degree of pollution the Earth can stand.

My interest and thereby my aim in this interdisciplinary field has been to provide scientists, primarily atmospheric chemists and meteorologists, with new tools to gain a new and deeper understanding of the effects on nature by atmospheric anthropogenic pollutants. This thesis deals, of course, with a very limited part of the whole field. It is also of importance in this context to stress that in the handling of pollution problems is not only important to gain knowledge about them but also to take action against the problem.

The introduction of a fast multielemental technique (PIXE) for the analysis of elements heavier than aluminum has facilitated large scale aerosol studies. The properties of PIXE (described later) make it very useful for producing large amounts of information concerning aerosol composition. The analytical method has to be combined with the appropriate sampling equipment to take the greatest possible advantage of the analytical method as well as to be able to answer the questions surrounding the nature of the atmospheric aerosol.

Information on aerosol source types and dominating source areas was gained using a combination of the multielemental features of PIXE and size-fractionated samples with good enough time resolution to allow correlation with meteorological data (paper I). More detailed information concerning the spatial dependence of the distribution of aerosol constituents with respect to meteorological parameters was obtained by using high time resolution, non-fractionating samplers in a network (paper II).

Multivariate statistical techniques were introduced and used to obtain the most possible information from the multielemental data base. The use of these techniques has led to significantly better understanding concerning the composition and transformation of anthropogenic releases (papers III and IV).

Further development of an aerosol sampler and a preconcentration technique for rain water was carried out to optimize the analytical and sampling system. Thus

Thus it will be possible in more extensive studies to follow the atmospheric aerosol, even in wet deposition (papers V and VI).

The PIXE-method

In 1970 Johansson, Akselsson and Johansson (1) at our laboratory proposed the use of accelerated charged particles to induce characteristic X-rays for X-ray spectroscopy in trace elemental analysis. This analytical method is today widely used over the whole world and is applied to many different fields such as environmental sciences, geology, biology and medicine. The proceedings of the three International Conferences on Particle Induced X-ray Emission and Its Analytical Applications, held in Lund (1976, 1980) and in Heidelberg (1983) show the development of the method as well as the extent of its applications (2 - 4).

The basic principle of the PIXE method is that vacancies are created in the electron shells of the atoms in a sample when bombarded by accelerated charged particles (protons or alpha-particles) in the MeV/u energy range. When the inner shell vacancies become filled with electrons from the outer shells X-rays with a certain energy characteristic of the element may be emitted. The probability of a certain element in the sample emitting characteristic X-ray for one bombarding proton is known. Thus, by measuring the energy and the intensity of the X-rays together with the number of protons the elements present in the sample can be determined quantitatively.

A typical experimental set-up can be described in short as follows. The sample mounted on a slide frame, to facilitate fast and simple sample changing, is placed in a vacuum and irradiated by accelerated charged particles from an electrostatic accelerator or a cyclotron. The area analysed, normally about $0,1\text{-}1\text{ cm}^2$, is determined by circular collimeters. The beam current used is normally in the 1-200 nA range. As many types of samples have major concentrations of light elements (e.g. Cl, K, Ca) different types of absorbers are used to reduce the intensity of the low energy X-rays from the light elements. The detector used is a semiconductor (Si(Li)) detector, which measures the energy of each X-ray. The X-ray spectrum is stored in a multichannel analyser. In routine analyses, 10 to 20 elements can be determined simultaneously with detection limits of the order of $10\text{ }\mu\text{g}$ in a thin sample ($< 1\text{ mg/cm}^2$) after a 1-3 minute radiation. When the detector is placed outside the vacuum system, the attenuation of the low energy X-rays in the chamber window sets a lower limit on the atomic number and only elements heavier than aluminum can be analysed quantitatively.

Thesis:

The aim of this work has been to apply the PIXE (Particle Induced X-ray Emission) method for analysis in an interdisciplinary field of atmospheric chemistry, meteorology and aerosol physics applied to atmospheric pollution problems.

The thesis can be summarized in the following points:

- a) The use of PIXE with suboptimized sampling equipment to gain knowledge about the elemental composition in different size fractions of atmospheric background aerosols with special emphasis on the larger sources and their influence.
- b) Development of evaluation techniques to make the most possible use of the multielemental information obtained with PIXE.
- c) Development of aerosol sampling techniques, which are optimized for PIXE analysis, and a preconcentration method for rain water, in order to be able to follow the wet deposition of the atmospheric aerosol.

Paper I

This paper describes a background aerosol study, carried out in Sweden, over a whole year. The high sensitivity of PIXE for very small samples makes it possible to measure the elemental concentration for normally 10 to 15 elements with high size resolution over a period of 24 hours, which allows for meteorological interpretation. The sulphur and heavy metal concentration for the 113 samples were orders of magnitude lower than in central Europe, but only a factor of two to four higher than the winter concentration in the Arctic. The size distributions were found to be in line with possible source processes. The air masses were classified according to air mass trajectory analysis, to reveal the large source areas. Up to an order of magnitude higher concentrations of known anthropogenic components, e.g. S, V, Ni, Cu, Zn and Pb were found in air masses, which had traversed the British Isles or central Europe compared with air masses originating in the north Atlantic.

By applying a simple box model and from estimations of the Swedish emissions, the foreign contribution to the elemental concentrations could be estimated for S and Pb to between 70 and 80 %, 50 % for Ni and 30 % for V. The seasonal

variations were found to be greatest for the anthropogenic components, except sulphur. Wet deposition was found to be dominant for mainly anthropogenically derived elements.

Paper II

To obtain better information on the spatial and temporal patterns of long-range transport episodes, when occurring in southern Sweden, a sampling net was set up and operated. Four rural and one urban station (Stockholm) were placed in a direction east-north-east in a line from Gothenburg to Stockholm (distance 500 km). A southerly rural station was placed in the very south part of Sweden, about 450 km south of the other stations.

Good time resolution was achieved by using the Florida State University time sequential filter sampler, which is a light, rather simple total filter sampler, designed especially for PIXE. By using surface weather maps and air mass trajectories as well as elevated sulphur concentrations, two episodes were clearly identified. The temporal variation in the concentration of sulphur at the different sampling sites made it possible to see the spatial extension of an episode. The ratios of S to V and Ni respectively were used to identify local influences.

Paper III

To extract as much information as possible from a multielemental data base a new multivariate statistical technique, combining principal component analysis with pattern recognition, is demonstrated. This computer program package, called SIMCA, was used to evaluate the elemental concentrations in the accumulation mode from a data base, presented in paper IV.

Before attempting any statistical analysis it is important that the data be carefully normalized and scaled. These procedures are also described.

As a result of the multivariate statistical analysis it was found that the southerly air masses, originating from central Europe, have a low variability in fine mode elemental composition being clearly different from the northerly air masses.

Paper IV

A more extensive study of transformation and deposition mechanisms of the atmospheric aerosol, occurring during a long-range transport episode over southern Sweden is presented in this paper. A small network, two coastal (south and west coasts) stations and one inland station, with cascade impactors was operated. Air mass trajectory analysis was used to classify the different samples into northerly and southerly sectors. Compared with elemental concentrations presented in paper I, the results obtained in this study for different sectors, agree well. Inter-station comparisons of fine mode elemental concentrations measured simultaneously, provide a method for the calculation of the foreign contribution to the elemental concentrations, not based on emission data, and give results in good agreement with those reported in paper I. The multivariate statistical method described in paper III is further used in the analysis of elemental concentrations in different size fractions of the accumulation mode. Separation of the elemental composition between the different size fractions is clearly seen revealed at all stations. Within a size fraction no significant separation is seen between the different stations. Elements such as S and V (or Ni) normally assumed to originate from the same sources, were already separated and S clustered with K, Mn and Zn. This was interpreted as being due to the transformation of SO_2 to hygroscopic particles rich in K, Mn and Zn being more probable than the transformation to non-hygroscopic particles rich in V and Ni.

Paper V

Wet deposition of the anthropogenic elements in the atmospheric aerosol was found in paper I to be the most important deposition process. To be able to make accurate determinations of the heavy metals in the atmospheric aerosol, it is necessary to carry out continuous sampling and analysis of rain water, to obtain an appropriate estimate of the deposition.

A non-selective preconcentration technique for rain water was developed facilitating a fast multielemental analysis with PIXE. The water is nebulized in a concentric nebulizer. Thus a polydisperse water droplet aerosol is formed. This is dried with particle free dry air. The dry aerosol is then collected in an impactor on a thin polystyrene foil, which is a very suitable backing for PIXE analysis. An appropriate amount of rain-water for preconcentration is 10 ml. The drying procedure then takes about 30 minutes. The detection limits are of the order of $0.1 \mu\text{g/l}$, with which it is expected to detect about 25 different

elements in normal rain-water.

Paper VI

From the investigations earlier described and from other studies, especially concerning the physical properties of the atmospheric aerosol, it was found that two size fractions would be enough for both hygienic studies and to determine the source type. Bearing this in mind a highly automatized two stage aerosol sampler, designed especially to suit PIXE, was constructed. The aim was also to optimize the total sampling and analytical system both for long-term monitoring and intense sampling campaigns.

The presented prototype has a capacity of 70 samples at the maximum flow rate (5 l/min). The coarse particle fraction is collected on an impactor stage and the fine particles on a filter after the impactor. A new type of impaction surface has been developed, which reduces the bounce-off losses to about 5 %, even at high mass loadings. The impactor nozzle is changeable and thereby the cut-off between coarse and fine mode is easily changed. The sampler is constructed to give high flexibility to fulfil the given demands of particular sampling situations. The sampler is controlled by a dedicated microcomputer to allow the greatest possible freedom in choosing sampling strategy. The computer also checks the flow rate and takes the appropriate action if it is outside a preset range.

Tests with well defined laboratory aerosols were performed to investigate internal losses, impactor characteristics and filter efficiency and are presented. The total losses, including wall losses, bounce-off and filter leakage, were found to be in the 5 to 15 % range for particle sizes between 0.05 and 10 μm diameter.

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To be published in Nucl. Instr. and Meth.

ACKNOWLEDGMENTS

This thesis is the direct result of inspiring and for me very important team work. I do not know how to express my gratitude towards all people who have participated in this work or who have supported me not only in the work with the specific papers presented in this thesis but also in instructing me in the areas covered in this interdisciplinary thesis. I will anyway make an attempt to express my thanks to:

Roland Akselsson, who with great patience and understanding, has been my supervisor and teacher. Without his support and encouragement much of this work would never have been done.

Sven A. E. Johansson, for his understanding and interest in the development of different applications of the PIXE method.

Hans Lannefors, my closest companion in several projects, a never hesitating and untireable cooleague.

The whole PIXE group; former as well as present members; Mats Ahlberg, Mats Bohgard, Lars-Eric Carlsson, Ann-Kristin Ekholm, Eva-Marta Johansson, Gerd Johansson, Katarina Johansson, Li Hong-Kou, Klas Malmqvist, Bengt Martinsson, Stefan Nyman, Jan Pallon, Pirjo Pakarinen and Erik Swietlicki, who together form a group of most helpful and inspiring people, which has been very important for me and my work.

Lars Berne Nilsson, Preben Jensen, Erik Karlsson and Knut Sjöberg, all very skilful and creative in constructing the analytical facility and the aerosol samplers.

Ragnar Hellborg, Kjell Hellborg and Christer Nilsson for providing technical assistance and a well maintained accelerator.

Britt Hansson, for excellent drawings
Britt-Marie Kallerhed, our most helpful secretary
Rose-Marie Akselsson, for excellent typing
Jörjen Raquette, our skilful carpenter
and Helen Sheppard, who translated my swenglish to english.

There are also many people outside the department who have been important in my

work. I would like to mention,

Jost Heintzenberg, Lennart Granat and Henning Rohde at the Department of Meteorology, University of Stockholm for very fruitful collaboration.

Lennart Persson at the often-used sampling site, Sjöängen, and other people who have kindly assisted in the field work in our studies,

and, of course, my nearest and dearest for love and support.

This work has been partly supported by the National (Swedish) Environment Protection Board.

BACKGROUND AEROSOL COMPOSITION IN SOUTHERN SWEDEN—FOURTEEN MICRO AND MACRO CONSTITUENTS MEASURED IN SEVEN PARTICLE SIZE INTERVALS AT ONE SITE DURING ONE YEAR

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Abstract The aerosol composition as a function of particle size, has been studied at a rural location in southern Sweden, during a period of one year. The sulphur and heavy metal concentrations have been measured in 113 cascade impactor samples by particle induced X-ray emission (PIXE). Elemental concentrations were orders of magnitude lower than in central Europe but only a factor of two to four higher than the winter concentrations in the Arctic. The size distributions were rather broad except for some of the anthropogenic components. Enrichment factors calculated in both the fine and coarse particle mode gave information on possible anthropogenic contributions in the fine mode for the expected soil derived elements K and Mn. The samples were classified according to calculated air mass trajectories. Air masses having traversed the British Isles or central Europe contained up to an order of magnitude higher concentrations of known anthropogenic components e.g. S, V, Ni, Cu, Zn and Pb than air masses originating in the north Atlantic. The foreign contribution of the elemental concentrations was estimated to 70–80% for S and Pb, 50% for Ni and 30% for V. The anthropogenic components (except sulphur) showed the largest seasonal variations being highest in the winter. Dry deposition estimates indicate that the wet deposition was dominant for the fine particle oriented elements (S, V, Ni, Cu, Zn and Pb), while for the large particle oriented elements Ti and Fe dry and wet deposition were of equal importance.

An appendix concludes this paper and presents elemental concentration frequency distributions in the fine and coarse mode

INTRODUCTION

Aerosol studies using the PIXE-analysis technique in combination with suitable sampling devices such as filter, streaker or cascade impactor samplers present great opportunities for large-scale aerosol composition measurements. This study includes 113 sets of samples taken with a 7-stage cascade impactor, giving information on 10–20 elements (of which 14 are presented here) on each stage which results in approximately 11,000 data points. In this paper, we intend to give an overview of the large data set. We will, therefore, concentrate on a discussion of the results in terms of yearly and seasonal elemental concentration averages as well as averages calculated according to the history of the air mass. A discussion of the calculated contribution from Swedish and Finnish sources, the average enrichment factors and the dry deposition is also included. In an appendix, the frequency distributions of the elemental concentrations in the coarse and fine particle mode are shown.

Measurements of trace element concentrations in different particle size fractions of the atmospheric

aerosol at rural and remote locations (100 to several thousand km from major source areas) have not been carried out very extensively. Rahn (1971) reported data from Canada on elemental composition in five particle size fractions. Size-segregated samples from rural locations in Great Britain were obtained during many years and analysed for several trace metals (e.g. Cawse 1974). Flocchini *et al.* (1976) studied particle size distribution and elemental composition of California's aerosol at 13 urban and non-urban sampling sites. Johansson *et al.* (1976) obtained cascade impactor samples from a number of coastal and inland stations in Florida. The relation between sulphur concentration and other trace elements in South America was determined by Lawson and Winchester (1978). Crustal reference elements in non-urban aerosols were studied as a function of particle size by Lawson and Winchester (1979). All these studies except Rahn's and the U.K. measurements were based on the PIXE analysis technique although the sampling methods were different.

The long-range transport of some man-made air pollutants is now of common and widespread interest.

Publications by Bolin (1971), Brosset and Åkerström (1972), Rodhe *et al.* (1972), Bolin and Persson (1975), Brosset (1976) and the OECD/LRTAP study 1973-1974 (OECD, 1977) have led to a general recognition of long-range transport with particular emphasis on sulphur. Much less is known about the long-range transport of micro components, typical concentrations in rural locations and amounts deposited in, for example, Sweden. Systematic moss analysis (e.g. Rühling and Skårby 1979) gives valuable qualitative information. Some measurements of aerosol trace metal concentrations at rural locations in Scandinavia have been performed (e.g. Semb, 1979; Heintzenberg and Trägårdh 1979; Laveskog and Thorsmark, 1979). However, the study presented here is probably the most extensive so far in this area.

EXPERIMENTAL

The sampling site (Sjöängen) is located between Lake Vänern and Lake Vättern (Fig. 1) within a representative basin for the Swedish programme within the International Hydrological Decade. It is also the site for regular meteorological and atmospheric chemistry measurements, some of them part of a national Swedish programme for the supervision of environmental quality. The area is described in more detail in Hydrological Data-Norden (1976). The nearest city is at a distance of about 30 km. Larger cities (> 100,000 inhabitants) and areas with many industries are found some 200 km from the site (see Fig. 1), except for one smelter which is 110 km southwest of the sampling site. The distance to the nearest agricultural field is about 1 km while larger farming areas are more than 10 km away. There is a small road nearby having a very low traffic intensity (< 10 vehicles day⁻¹).

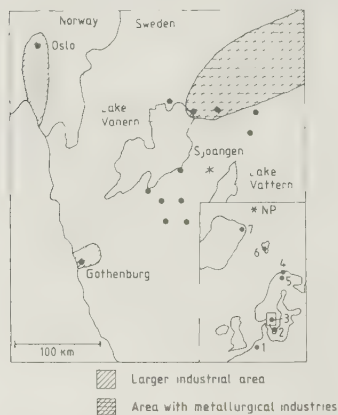


Fig. 1. Map showing the location of the sampling site (Sjöängen), some major cities (Gothenburg and Oslo with several hundred thousand inhabitants) and the nearest cities (having up to 100,000 inhabitants). Major industrial areas are indicated. The referenced sampling locations in Table 2 are also pointed out.

Parallel measurements at this site and another site at 3 km distance, with two nephelometers during several months, indicate that the site is practically free from local contribution to aerosol volume in accumulation mode.

The sampling device was placed on top of a tower 17 m above the ground, in an area which is cleared from trees and mainly covered with grass. The sampler is a cascade impactor of Battelle design (Mitchell and Pilcher, 1959) with a flow rate of 1 l min⁻¹ and with the following size fractions given for aerodynamic diameter (of unit density): < 0.25, 0.25-0.5, 0.5-1, 1-2, 2-4, 4-8 and > 8 µm. The stage collecting particles less than 0.25 µm consists of a 0.4 µm pore diameter Nucleopore filter having an efficiency (at 50% vacuum) estimated to be better than 80% for all particle sizes. Bounce-off was kept low by using a paraffin coating on the impaction surface (Lawson, 1980) and avoiding high loading of sample material. The large particle intake efficiency of the impactor and cover varies with the wind speed and the first stage (> 8 µm) was consequently only used to give an upper particle size limit. The material found on this stage was not further evaluated and, therefore, "total" concentrations in the following are referring to concentrations on particles less than 8 µm dia. It should be noted that at high wind velocities the intake efficiency for particles finer than 8 µm might also be affected. However, the large particle intake efficiency can be increased by employing a turbulence inducing sampling hood (in this study a conical hood was used). This was found by Pattenden and Wiffen (1977) in laboratory experiments and by May *et al.* (1976) in a field experiment. Furthermore Benarie (1977) has compared a low and a high volume sampler (the latter often expected to have a higher intake efficiency) with rather similar sampling heads in an urban and a laboratory study. In the latter study, silica dust with aerodynamic diameters in the 2-50 µm range were used. No significant concentration differences between the two samplers were found. Based on these studies we believe that the loss in the particle intervals below 8 µm are not of such a magnitude that they would affect the conclusions drawn in this paper.

Samples were taken every day during a 1-y. The sampling time, 24 h, is usually long enough to provide sufficient material for a satisfactory analysis and short enough to permit a detailed interpretation with regard to meteorology and long-range transport. Elemental analyses were made by particle induced X-ray emission (PIXE: Johansson *et al.*, 1975). Samples collected during the first 5 months of the project were analysed using beams of 2 and 3 MeV protons generated by the Van de Graaff accelerator at the Niels Bohr institute in Copenhagen, Denmark. The remaining samples were analysed using a beam of 2.5 MeV protons from the Pelletron accelerator at the Department of Nuclear Physics, Lund Institute of Technology, Lund, Sweden. The radiation time was approximately 3 min per sample. Spectra were evaluated using a computer code developed by Kemp (in Copenhagen) and by Kaufmann (in Lund; Kaufmann *et al.*, 1977). The accuracy and precision of the PIXE analysis is usually 10-15%. For a limited number of samples which were slightly overloaded the uncertainty, however, is higher because of corrections for the X-ray absorption and losses in the impactor. The reproducibility of the sampling is about 15% (van Grieken *et al.*, 1976). The overall uncertainty (one standard deviation) in most of the individual concentration estimates is therefore of the order of 25% or less which is low compared to the observed day-to-day variations in elemental concentrations.

DATA PRESENTATION AND INTERPRETATION

Elemental concentrations and their variability

We start the presentation with a statistical summary of the concentration distribution for the fine (< 1 µm) and coarse (1-8 µm) particle modes (Table 1 and

Table 1. Statistical summary of elemental concentrations at Sjöängen based on 113 sets of 24-h measurements during one year. T, F and C refer to particle size intervals of < 8, < 1 and 1–8 μm , respectively. The values are given in ng m^{-3} .

	Arithmetic mean			Lower quartile			Median			Upper quartile		
	T	F	C	T	F	C	T	F	C	T	F	C
S	800 (680, 110)			240 (190, 32)			480 (390, 83)			1100 (920, 130)		
Cl	190 (25, 160)			18 (< 4.5, 7.6)			55 (12, 32)			190 (27, 180)		
K	76 (46, 30)			35 (17, 13)			50 (32, 22)			100 (60, 39)		
Ca	74 (18, 56)			28 (6.7, 18)			59 (12, 42)			110 (22, 73)		
Ti	5.0 (1.4, 3.6)			1.6 (0.52, 0.93)			3.4 (0.87, 2.3)			7.0 (1.7, 5.1)		
V	2.5 (2.1, 0.38)			0.68 (0.61, < 0.060)			1.5 (1.4, 0.19)			3.9 (3.1, 0.63)		
Cr	2.8 (1.9, 0.83)			1.2 (< 1.0, 0.13)			2.0 (1.4, 0.47)			2.9 (1.9, 1.1)		
Mn	6.7 (3.9, 2.8)			2.5 (1.1, 0.85)			4.5 (2.6, 1.7)			9.5 (5.2, 3.8)		
Fe	88 (34, 53)			3.0 (9.5, 15)			48 (18, 29)			140 (55, 70)		
Ni	1.5 (1.2, 0.36)			0.60 (0.44, < 0.060)			1.1 (0.84, 0.22)			2.1 (1.6, 0.45)		
Cu	2.4 (1.8, 0.54)			0.59 (0.40, < 0.075)			1.1 (0.79, 0.23)			2.8 (2.2, 0.59)		
Zn	24 (16, 7.5)			5.0 (3.9, < 0.24)			15 (10, 3.0)			37 (26, 10)		
Br	2.8 (2.0, 0.71*)			0.85 (< 0.55, < 0.30)			2.4 (1.8, < 0.30)			3.8 (2.8, 0.88)		
Pb	21 (17, 4.0)			6.8 (5.6, < 0.75)			12 (11, 2.1)			32 (26, 5.5)		

* More than 50% of the values below the detection limit.

appendix). Attempts have been made to fit a bimodal log-normal size distribution to individual elemental concentration particle size distributions using non-linear regression (Hansson and Lannefors, 1980). The impactor cut-off characteristics were thus taken into account. This procedure gave consistent results for stage-wise sums of the elements but was not successful for individual elements. The division between the fine and coarse particle mode made in Table 1 is one of many possible ones. In a following section the size distribution will be studied in more detail.

The frequency distribution of elemental concentrations (shown in the appendix) cannot be described with a simple mathematical expression valid for several components although some elements show a tendency to a log-normal distribution. We have, therefore, chosen to present both medians and arithmetic means since both of them have their special merits. The variability is shown by quartiles. The wide range in concentration is apparent; 75% of the cases are roughly between 1/4 and 4 times the median value and cover a range of more than two orders of magnitude between the few highest and the few lowest values for most components both in the fine and coarse particle modes.

The amount of material collected is sometimes too small for reliable analysis. When this is the case, a concentration half the value of the detection limit is assigned to the sample (detection limit here taken to be three times the square root of the X-ray background or half the filter blank whichever is the greatest). For some elements this occurs quite frequently at some impactor stages. It should be noted that if a geometric mean value is calculated in these cases, it is heavily dependent on the assigned value.

Comparison between concentration at Sjöängen and at some other locations

The concentration levels at Sjöängen lie well within

the range of values found on the European continent and in the Arctic (see Table 2). Concentrations of all components except sulphur and nickel are between one and two orders of magnitude higher in Holland. On the other hand late winter concentrations at Spitsbergen (typical for the Arctic winter) and yearly mean concentrations at Jergul and Lakselv (northern Norway) are typically a factor of two to four lower than at Sjöängen. Arctic summer values (Greenland) are even lower. Distances to major source areas range in these cases from 1000 (Sjöängen), 2000 (N. Norway) to 3000–4000 km (Spitsbergen and Greenland). Sulphur has the smallest relative difference in concentration when comparing sampling sites close to major source areas with those furthest away while some primary aerosol constituents, most probably of anthropogenic origin (e.g. Zn and Pb), show a more rapid decrease with distance. Some components, primarily of crustal origin like Fe, show only a small variation between the sites except in Holland.

Distribution of elements in particle size intervals

Arithmetic average concentrations were calculated for each element in each of the 7 particle size intervals and the result is given in Fig. 2. The distribution below 0.25 μm is unknown and we have, for convenience, assigned a lower limit of 0.06 μm . The size of the area below 0.25 μm is thus based on measurements although its shape is unknown. The mass median diameter is below 0.5 μm for V and Cu, between 0.5 and 1 μm , in increasing order, for Pb, S, Ni, Zn, K and Mn and between 2 and 4 μm for Ti, Ca and Cl. In fact, more than 3/4 of the mass is found in particles less than 1 μm for the first 5 elements while for Mn and Zn the corresponding limit is about 2 μm . The elements Cl, Ca, Ti and Fe have on the other hand about 3/4 of the mass in particles larger than 1 μm . One can, in fact, regard size distribution of several components as a

Table 2. One year average concentration at Sjöängen compared to elemental concentrations measured at some other selected sites (see Fig. 1). Unit ng m⁻³

	Maassluis ¹ Holland	Boalt ² southern Sweden	Sjöängen ³ this work	Lakselv ⁴ northern Norway	Jergul ⁵ northern Norway	Ny-Alesund ⁶ Spitsbergen (winter)	Northern Greenland (summer)
degr N	52	56	59	70	69	79	82
S	3700	1600	800	—	720	690	27
Cl	1500	1000	190	290	—	—	10
K	850	160	76	48	—	32	3.8
Ca	—	150	74	46	—	73	9.1
Ti	—	12	5.0	3.1	—	5.2	0.85
V	48	4.5	2.5	1.7	1.5	—	0.12
Cr	20	—	2.8	0.62	—	2.6	0.09
Mn	83	8.4	6.7	2.5	1.5	1.5	0.21
Fe	2100	110	88	51	—	64	6.4
Ni	0.2	2.7	1.5	1.3	—	0.7	0.08
Cu	200	4.6	2.4	2.3	—	1.9	—
Zn	420	24*	24	8.9	6.0	3.2	0.18
Br	160	—	2.8	4.7	—	—	0.29
Pb	—	32	21	5.5	6.4	4.9	0.20

¹ One day samples (18) taken during one year (Evendijk, 1974).² Weekly samples taken during 3 summer months and 1 winter month (Wiman and Lannefors, unpublished work).³ 24-h measurements every third day during one year (this work).⁴ Weekly samples taken during one year (Rahn, personal communication).⁵ Two-day samples taken continuously during one year (Hanssen *et al.*, 1980).⁶ Two to five day samples taken continuously during 3 late winter weeks (Heintzenberg *et al.*, 1981).⁷ Two to seven day samples taken during 2 summer months at Kap Harald Moltke (Flyger and Heidam, 1978).

* Based only on measurements during one winter month.

combination of typical spectra for fine and coarse particle oriented components. This is especially obvious in the case of K but also for instance for Fe. The size-distributions for Cr and Br are not included since detected concentrations normally only occur on one or two stages. It should be remembered that only particles with an equivalent aerodynamic diameter less than 8 µm are included in these calculations.

These size distributions are in line with previous findings and possible source processes such as combustion, soil erosion and seaspray and will be further discussed in a following section.

Enrichment factors

Enrichment factors have been used rather extensively to indicate which elements have sources in addition to natural ones (mainly sea-spray and soil erosion). Fractionation effects have been found to alter the relative composition of elements from that in the bulk material (e.g. Rahn, 1976; Lawson and Winchester, 1979; Garland, 1981). Used with caution the concept may still be useful and enrichment factors with titanium as reference element are given in Table 3. The use of particle size fractionating samplers in combination with sensitive analytical techniques has assisted the interpretation of source types from elemental size distributions. Assumptions that anthropogenic emissions are mainly found in the accumulation mode while natural emissions are mainly found in the coarse mode have thus been made. The average

enrichment factors are calculated according to:

$$E = \frac{1}{113} \sum_{i=1}^{113} \frac{X(\text{aerosol})/\text{Ti}(\text{aerosol})}{X(\text{soil})/\text{Ti}(\text{soil})}$$

Titanium was selected as the reference element in this data set since it is likely that anthropogenic sources (mainly smelters) contribute relatively more to Fe than to Ti. From the scatter diagrams in Fig. 3 it can be seen that the Ti and Fe concentrations in the coarse mode are very closely related. The slope of the line in the figure represents the ratio between Ti and Fe according to Bowen (1966). Assuming no fractionating effects, as

Table 3. Average enrichment factors in the fine and coarse modes and for the total concentrations, calculated using the average soil composition given by Bowen (1966)

	Fine (< 1 µm)	Coarse (1-8 µm)	Total (< 8 µm)
S		480	1400
Cl		12000	5200
K	16	6.2	8.3
Ca	6.0	11	7.4
Ti	1.0	1.0	1.0
V		11	36
Cr		30	54
Mn	19	8.7	11
Fe	3.1	3.3	3.2
Ni		29	61
Cu		70	160
Zn		300	560
Br		750	2700
Pb		1100	2800

the enrichment factor for Fe is around three, there is an indication that Fe might have larger additional sources than Ti. If the reference element has non-soil-derived components of the same order of magnitude or larger as the soil-derived component it is not meaningful to calculate enrichment factors. This is more likely to occur in the fine mode than in the coarse mode. From this data set it cannot be concluded whether or not such sources exist.

Enrichment factors in the fine mode ($< 1 \mu\text{m}$) are only given for potentially soil-derived elements. These

enrichment factors point to at least K and Mn having additional sources for particles in this interval. The remaining elements in Table 3 all have high enrichment factors (80–8000) in the submicrometre range which indicate dominating anthropogenic or other natural sources. In the particle interval $1\text{--}8 \mu\text{m}$, Fe and possibly also K, Ca, V and Mn, have the same source as Ti (soil dust). The enrichment factor is much higher for the rest of the elements listed, indicating that other sources must also contribute in this interval. Whether these high enrichment factors are caused by condensa-

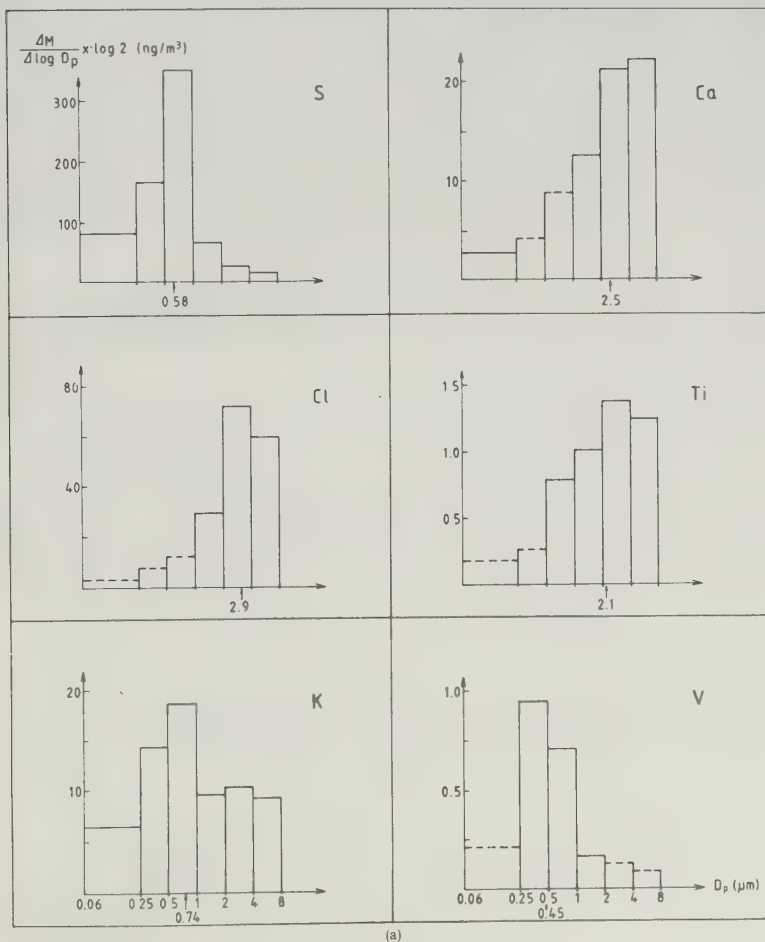
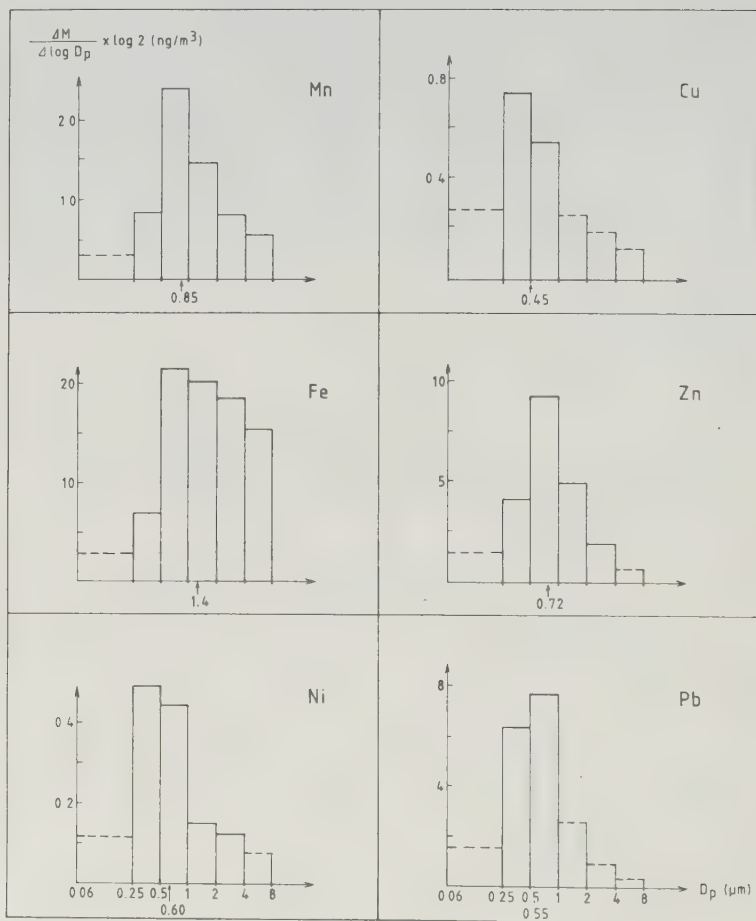


Fig. 2(a).



(b)

Fig. 2. Particle size distributions of the elemental concentrations. The diagrams show the average concentration per logarithmic particle size interval vs the logarithm of the diameter. The numbers given on the ordinate are actual concentrations except for the $0.06\text{--}0.25 \mu\text{m}$ interval where the actual concentrations are obtained by multiplying the ordinate concentrations by two. The numbers by the arrows are the mass median diameters (equivalent aerodynamic diameter in μm) for each element. In the intervals having broken lines more than 50% of the values are below the detection limit.

tion or coagulation reactions in the atmosphere or on the ground, or whether, fractionating effects exist cannot be concluded. The high enrichment factor for Cl is probably caused by sea spray. Enrichment factors for the whole size range (up to $8 \mu\text{m}$) are also given in Table 3 for comparison with earlier enrichment factors obtained from total filter measurements.

Comparisons of the enrichment factors in the two size intervals can give additional information to resolve whether a specific element has additional sources or if the colian soil dust composition used is non representative. As mentioned earlier, K and Mn probably have additional sources contributing to the fine mode while not so strong indications of additional

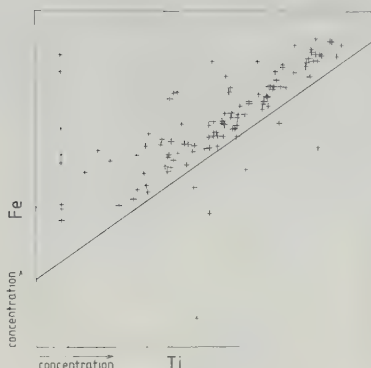


Fig. 3. Scatter diagram of Ti vs Fe in the coarse (1–8 μm) particle mode.

sources are found in the coarse mode. Fe has almost equal enrichment factors in both modes indicating the non representativeness of the soil composition used but can also be the result of fractionation effects.

Sector analysis

The samples were grouped according to the history of the corresponding air parcel. For a proper classification the following information was considered:

- (i) 48-h back trajectories for every six hours at the 850 mb level (obtained through the Norwegian Institute for Air Research).
- (ii) Daily synoptic surface weather maps covering northern Europe (issued by the Swedish Institute of Meteorology and Hydrology).
- (iii) Recordings of the local weather situation at the sampling site.

Samples obtained during reasonably stable (in time) conditions were assigned into one of the five sectors shown in Fig. 4. About 30% of the cases could not be classified in this way because of undefined trajectories or that the trajectories passed over several sectors.

The borders of sector 1 are carefully selected so that this sector only contains "clean" air samples (i.e. low sulphur values). It was not possible to obtain a well defined border between sectors 1 and 2 and we have consequently located a "buffer" sector (B) between 1 and 2 which contains both rather "clean" and "polluted" samples while most of the samples in sector 2 show high concentrations of air pollutants. The divisions between sectors 2 and 3 and between sectors 3 and 4 are less critical. Sectors 2 and 3 are intended to show air pollutants from west and east of Europe, respectively. Sector 4 is most likely dominated by sources in Sweden with some contribution from Finland and the Leningrad area. This will be discussed below. The width of sector B (20 degrees) can be regarded as an estimate of the precision in trajectory calculations. It must be remembered that there is a

limited number of samples in each group (about 15) and that some bias can occur with regard to source strength and dilution capability (since time of the year, windspeed and other factors are not evenly distributed between sectors as shown below).

The mean concentration of each element in each sector is shown in Fig. 4 and does (to some extent) reflect the relative source strength in the sector weighted by distance. The elements Cr and Br are not included since their values are very close to or below the detection limits in sectors 1 and 4 and are, therefore, very uncertain.

We can distinguish at least three different patterns in Fig. 4 with regard to the dependence of trajectory direction. Sulphur shows the strongest directional dependence—really low concentrations in sector 1, high in both sectors 2 and 3 and rather low in sector 4. For Cu, Zn and Pb the concentrations in sector 1 and 4 are also much lower than in sector 2 which is also somewhat higher than in sector 3. K, Ca, Ti, V, Mn, Fe and Ni have a weaker directional dependence, about equal concentrations (especially in the accumulation mode) for most of these elements in sectors 1 and 4 and lower than in sector 2 which is here somewhat lower than in sector 3. Concentration of Cl in the accumulation mode is essentially independent of trajectory orientation.

For Ca, Ti and Fe in the coarse particle mode we notice that the concentration is about equally high in sectors 2 and 3, a factor 2 lower in sector 4 and still lower in sector 1. It is also interesting to note that the directional dependence is not the same for the sub-micrometre fraction of these components—here concentration in sector 3 is almost twice that in sector 2. In the coarse particle mode chlorine has high concentrations in sector 1 (and in the buffer sector) which is to be expected with the Atlantic as a strong source.

Comparing sectors 2 and 3 (west and east of Europe) we find no major differences. The sulphur concentration is for instance almost the same. If anything, Cu and Pb seem to be somewhat higher in sector 2 while V and Ni are somewhat higher in sector 3. With regard to possible bias and the influence of Swedish sources discussed in the following paragraph we cannot infer any differences in emission profile between the west and east of Europe from the present study.

The relative contribution from each sector to the grand average concentration for some elements is given in Fig. 5 which thus shows the relative importance of sources in a particular sector when the frequency of occurrence (see Table 4) is also considered. The "undetermined" sector consists of samples taken during calm conditions or when a set of trajectories could not be assigned to a particular sector. This sector contributes most to the grand average. Air parcels with trajectories in sectors 2 plus 3 contribute 40–50% of the grand average for the elements S, Ti, Fe, Cu, Zn and Pb although the frequency of occurrence is only 23%. The high chlorine contribution from the buffer sector should be noted.

Contribution from Swedish compared to foreign sources

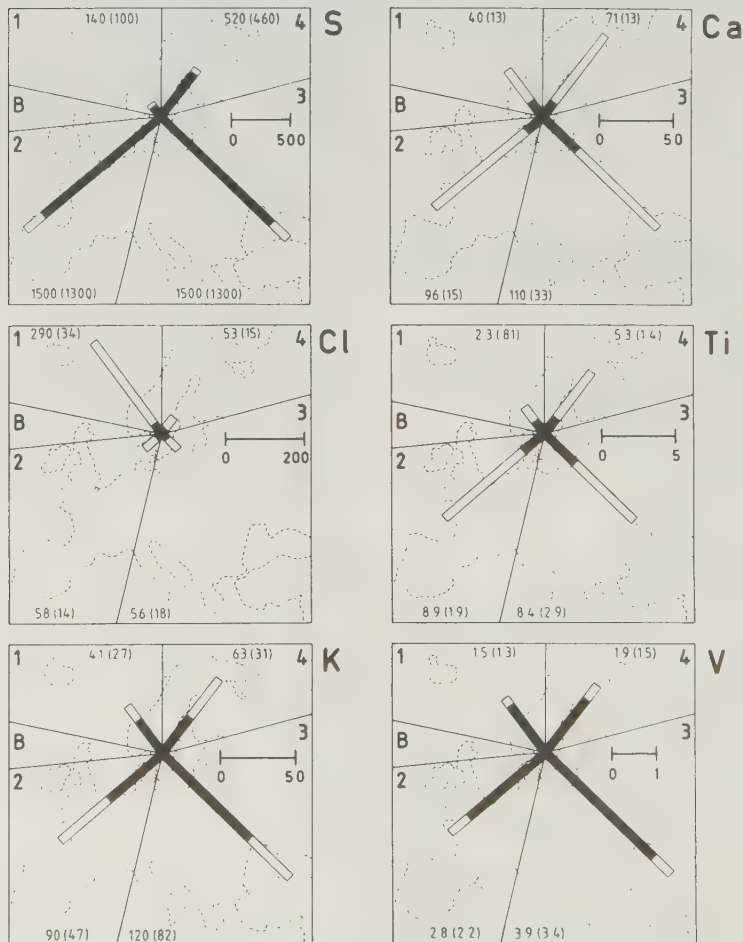
In a paper by Shaw (1981) a simple atmospheric dispersion model was applied to the data-set described in this paper. The model assumes that the emission from a source is spread and advected within a certain sector, well mixed within the atmospheric boundary layer. At a certain point the concentration is given by

$$c = \frac{Q(1-L)}{uH(\theta r + y)}$$

where Q is emission rate; L , loss term due to deposition, chemical transformation, etc.; u , horizontal wind velocity; H , height of atmospheric boundary layer; θ , dispersion angle; r , distance from source to measuring point and y , width of source perpendicular to wind direction.

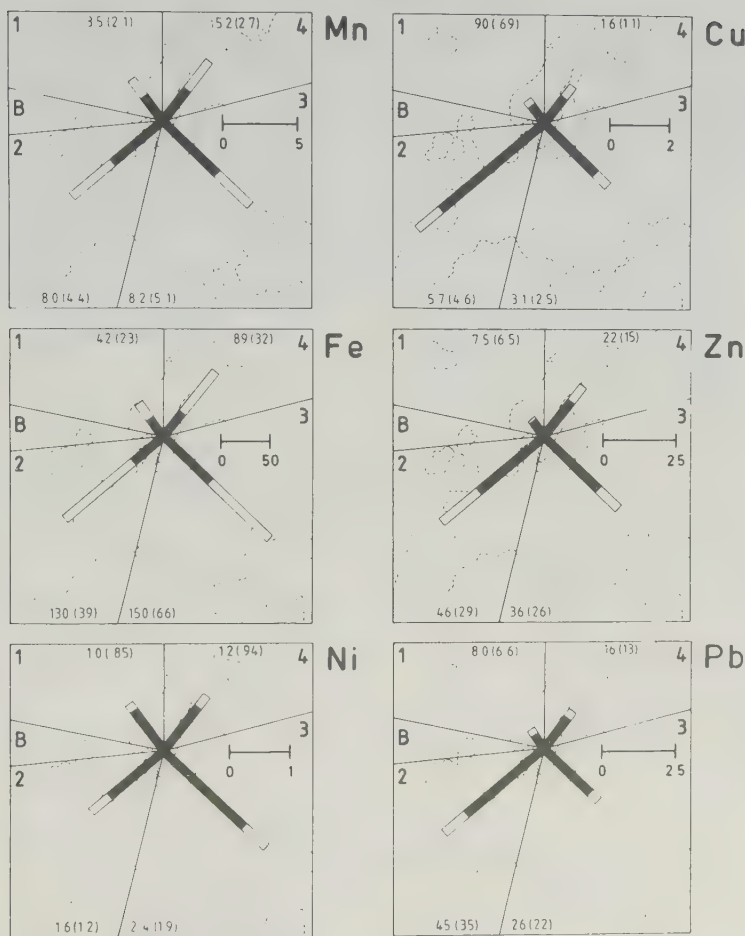
The following assumptions were used for the calculations:

$\theta = 0.5$ radians, $L = 0$ (except for lead where it was set to 0.2) and sector 4 concentrations were entirely the



(a)

Fig. 4(a).



(b)

Fig. 4. Average concentrations in four sectors. The filled part of the bar refers to the fine (< 1 μm) mode and the open part to the coarse (1–8 μm) mode. The numbers given are average total and within brackets fine mode concentrations (ng m⁻³) in each sector. Please note that different components have different scales.

result of emissions within Sweden except for S and Pb where Finnish sources were also considered.

The calculated concentrations for 11 of the samples (those with no precipitation) classified in sector 4 agreed with the measured concentrations within a factor of three for particles with a diameter less than 2 μm, see Table 5(a). The modelling technique was then applied without change to 13 of the samples classified

into sectors 2 and 3, see Table 5(a). Using these data and assuming no foreign (except from Finland) contributions in sector 4, a comparison was made between the average of the ratios of measured to calculated concentrations in sector 4 with those in sectors 2 + 3, see Table 5(b). The comparison suggests a substantial influence from foreign sources which is well above the uncertainties in the calculations. Swedish sources

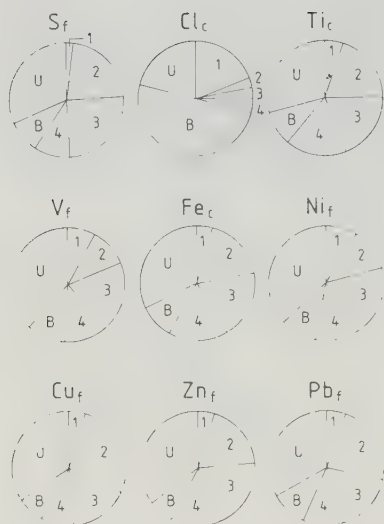


Fig. 5. Relative contribution from each sector for some of the components (in the fine (f) or coarse (c) mode) to the one year average concentration.

Table 4. Frequency of air masses in the different sectors

Sector	1	2	3	4	B*	U†
Frequency	12	11	12	16	17	32%
Angular fraction of sector	21	20	32	21	6	—

* Buffer sector.

† Unclassified samples.

included in the calculations can thus only account for 10–30% of the concentrations measured in the southerly air-masses (i.e. sectors 2 and 3).

In view of these results it may be of interest to calculate the contribution from Swedish sources to the yearly average concentration element by element.

Table 5(a). Average ratio measured/calculated concentrations in sectors 4 and 2+3

	S	V	Ni	Pb
Sector 4*	1.8	0.94	1.5	3.0
Sector 2+3*	19	3.9	6.4	10

* Based on 11 (sector 4) and 13 (sectors 2+3) selected samples taken during stable (in time) atmospheric conditions and when no precipitation had occurred in the air masses sampled.

Table 5(b). Approximate Swedish contribution in sectors 2+3 for particles < 2 µm—calculated from Table 5(a)

	S	V	Ni	Pb
Average Swedish contribution (%) in sectors 2+3	9.5	24	23	30

Based on the box model approach (basically the same concept as used by Shaw) the long-term average concentration C is obtained as:

$$C = \frac{Q(1-L)}{uHr2\pi}$$

where the following parameters have a different meaning than earlier defined

Q is yearly emission; u , average wind speed at 100 m and r = source strength weighted average distance.

The following assumptions (calculations) were used in the box model approach:

$L = 0$; $u = 5 \text{ m s}^{-1}$, $H = 1200 \text{ m}$ and $r = 260 \text{ km}$.

These numbers are chosen to overestimate rather than underestimate the contribution from Swedish sources. In the calculation of sulphur emissions 3% original conversion to sulphate and then $1\% \text{ h}^{-1}$ have been used. Thus, about 16% of the emitted sulphur is in the form of sulphate at the measuring site. The choice of $L = 0$ is a rough approximation, partly supported by discussion in a later paragraph. The results of the calculations are shown in Table 6.

The foreign contribution of sulphur to the wet and dry deposition in Sweden was estimated to be 70% in

Table 6. Comparison of the calculated and measured submicron concentrations at the Sjöäng sampling site giving the relative Swedish contribution

Element	Yearly* emission (ton y^{-1})	Calculated concentration (ng m^{-3})	Measured concentration (ng m^{-3})	Contribution Swedish sources (%)
S	250000†	130	680	20
V	460	1.5	2.1	70
Ni	180	0.59	1.2	50
Pb	1600	5.2	17	30

* References: S: K.H.M. (1981); V, Ni and Pb: Liedholm *et al.* (1981).

† Of which 16% is transformed to sulphate at the sampling site.

the OECD-report. In this report the calculations yield a value on the same level. In addition we also show that foreign sources play an important role for the concentrations in southern Sweden of some of the trace metals discussed in this work. This is in particular the case for Pb but to somewhat less extent also for Ni and V and is a result of the large emissions in central Europe and U.K., and a long enough residence time for the particulate material to be brought in over Sweden. Vanadium appears to have a somewhat lower relative foreign contribution than nickel. We cannot explain this difference though both V and Ni have their main sources in fossil fuel combustion, although fuel of different type and origin might be used. However, this difference is probably insignificant and can be regarded as an indication of the uncertainties in the calculations.

Seasonal variation in elemental concentration

A seasonal variation in elemental concentration can be expected as a result of changes in emission rates, transportation processes and dispersion efficiency during the year. The amplitude and phase of such variations can be expected to be rather specific for some groups of elements. In order to study the seasonal elemental concentration variation, mean concentration values were calculated for four periods: winter, spring, summer and fall. The sector classification of samples taken during the different seasons is given in Table 7. The fall season contained most cases with air masses originating in sector 2 or 3, in the year of sampling. Air masses arriving from the north Atlantic (sector 1) occurred least during the spring and summer while air masses in sector 4 occurred most frequently during the summer. Calm conditions and meteorological changes caused 37% of the summer

and winter samples to be "unclassified". As a measure of the "episodicity" the frequency of high values during each season was calculated (number of cases during a "season" with concentrations in the upper quartile of all cases), see Table 8. The highest frequency of such values for most of the anthropogenic components were found in the winter while only a few were observed during the summer. It is interesting to note that although the frequency of air masses from sectors 2 and 3 are highest in the fall, this is not reflected in a high episodicity as shown in Table 8 for this season.

Seasonal mean concentrations are shown in Fig. 6 and reveal a quite consistent picture. The lowest concentrations for almost all elements in both the fine and coarse modes were found during the summer. Most of the components of anthropogenic origin (high enrichment factors) show a substantial seasonal dependence with highest values in the winter, while most of the soil-derived components have a less pronounced seasonal variation with the highest values during the spring. The high ratio of winter to summer concentrations can be explained as principally due to meteorological factors, in particular a greater vertical dispersion in the summer, perhaps combined with somewhat higher emission rates during winter (at least for components associated with fossil fuel combustion) and a more efficient (incloud) removal rate during the summer. In the case of sulphur this effect (further enhanced by lower dry deposition of sulphur dioxide during the winter) is compensated by a much more rapid oxidation rate of SO₂ to sulphate during the summer. Also the soil-derived component may fit into this picture assuming a higher suspension rate during non-winter conditions but also a much more efficient (dry) removal rate. In the case of chlorine, a weaker source strength during the summer should also be considered.

Table 7. Seasonal frequency of samples in the different sectors

Sector	Winter	Spring	Summer	Fall	Total No.
1	6	2	1	5	14
2	2	1	3	6	12
3	3	4	1	6	14
4	2	6	9	1	18
Buffer	2	5	8	4	19
Unclassified	14	9	8	5	36
Total No.	29	27	30	27	113

Table 8. The seasonal "episodicity" of the total elemental concentrations defined as the number of cases in the upper concentration quartile of all samples for each element in each season

	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Winter	8	10	8	6	9	16	12	14	10	15	15	14	15	15
Spring	13	7	11	13	11	10	11	10	12	11	9	9	7	7
Summer	3	6	3	4	2	0	2	1	2	0	0	1	1	1
Fall	4	5	6	5	6	2	3	3	4	2	4	4	5	5

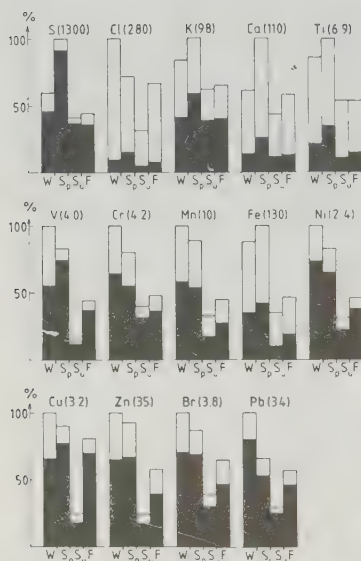


Fig. 6. Seasonal average elemental concentrations normalized to the highest concentration (given in brackets in ng m^{-2}) for each element. The filled part of the bars refers to the fine ($< 1 \mu\text{m}$) mode and the open part to the coarse ($1-8 \mu\text{m}$) mode. W denotes winter, S_p spring, S_u summer and F fall.

Dry deposition

The available data-base is well suited for an estimate of the dry deposition if combined with a so called dry deposition velocity (v_g). Ideally we need to assign values to v_g with regard to particle size distribution, ground cover and meteorological conditions. Such

Table 9. Dry deposition velocity used for estimating the dry deposition to a forest

Particle diameter (μm)	Deposition velocity (cm s^{-1})
0.06-0.25	0.3
0.25-0.5	0.2
0.5-1.0	0.3
1.0-2.0	0.5
2.0-4.0	1
4.0-8.0	4

values are not known with great accuracy even for a uniform area and well defined meteorological conditions and will, of course, be even more uncertain for long term averages for the real landscape. Extensive overviews (e.g. Sehmel, 1980) have demonstrated the uncertainty. For short vegetation and particle diameters of $0.1-1 \mu\text{m}$ predictions usually give values of less than 0.05 cm s^{-1} for v_g (i.e. Garland, 1977; Davidson and Friedlander, 1978; Sehmel, 1980). For $2 \mu\text{m}$ particles, for example, these authors give estimates of 0.06, 0.02 and 3 cm s^{-1} , respectively. For tall vegetation and accumulation mode particles Hicks (1980) summarizes: $v_g = 0.1 \text{ cm s}^{-1}$ represents the conventional viewpoint, $v_g = 0.4 \text{ cm s}^{-1}$ represents the most likely long term average for northwestern continental U.S.A., $v_g = 1.0 \text{ cm s}^{-1}$ is the highest value likely to be appropriate as a long term average over any normal surface in the continental U.S.A. For an estimate of the deposition velocity of particles larger than $1 \mu\text{m}$ diameter for tall vegetation we have essentially relied on work by Chamberlain (1975).

From a balance of evidence, from the literature and our own experience, we have adopted the numbers for v_g given in Table 9 as valid for a coniferous forest. They will be somewhat smaller for short vegetation. With the size distributions given in Fig. 2 we can now calculate a particle size weighted mean deposition velocity and then the yearly dry deposition (Table 10). Wet deposition to the same area is estimated from

Table 10. Estimated dry deposition to a forest compared to measured wet deposition

	Particle size weighted dry deposition velocity* (cm s^{-1})	Dry deposition ($\text{mg m}^{-2} \text{y}^{-1}$)	Wet deposition ($\text{mg m}^{-2} \text{y}^{-1}$)
S	0.40	100	900
Cl	1.8	100	500
K	0.86	21	100
Ca	1.6	38	200
Ti	1.4	2.3	5
V	0.45	0.35	3
Mn	0.72	1.5	6
Fe	1.1	31	20†
Ni	0.56	0.27	2
Cu	0.53	0.39	4
Zn	0.48	3.6	20
Pb	0.41	2.7	15

* For particles $< 8 \mu\text{m}$ dia.

† Very uncertain.

measurements at Sjöängen (Granat, unpublished data). Also considered are trace metal analysis in Denmark (Hovmand, 1979) and Norway (Semb, 1979).

Despite the uncertainty in the calculations we can conclude that for most of the elements the dry deposition is of less importance than the wet deposition, especially for those elements which have most of the mass in the accumulation mode (S, V, Ni, Cu, Zn and Pb) and also for Cl, K and Ca. For some of the large particle oriented elements, e.g. Ti and Fe, the dry deposition is on the same level as the wet deposition. In reality, the dry deposition may be larger since particles larger than $8\text{ }\mu\text{m}$ were not included in this estimate.

CONCLUSIONS

It was found that the 14 elements which were studied in this investigation could be conveniently divided into four groups each with the following characteristics:

(1) S, V, Ni, Cu, Zn, Pb and to some extent Mn have high enrichment factors relative to Ti and a strong seasonal variation with the highest concentrations during winter (except for S, where chemical reactions in the atmosphere counteract this variation). Most of the mass is found in the accumulation mode although there is some difference in the size distribution where V and Cu have the lowest median diameter and Mn and Zn the highest. The components are mainly of anthropogenic origin. We may not rule out that some of the submicrometre Ca, Ti and Fe may belong to this group although the indications are rather weak.

The highest concentrations and the largest relative contributions to the yearly averages for Cu, Zn and Pb occur in sector 2 (when the unclassified samples are not considered) which includes sources in western Europe. A similar comparison in sector 3 including sources in eastern Europe yields V and Ni. The sulphur concentration is about equally high in these two sectors.

The wet deposition is approximately one order of magnitude higher than the calculated dry deposition.

Swedish sources may contribute of the order of 1/4 to 1/2 to the yearly average concentration as found at Sjöängen for the elements S, Ni and Pb but some 2/3 in the case of V.

(2) Ca, Ti and Fe have low enrichment factors, most of the mass in the coarse particle mode ($1\text{--}8\text{ }\mu\text{m}$) and a weaker seasonal variation of the concentration with the highest values in the spring and the lowest values in the summer. The concentrations found in sectors 2 and 3 are on the same level which is a factor of two to four higher than in sectors 1 and 4. Dry deposition for Ti and Fe is on the same level as the wet deposition, while the wet deposition is dominant for Ca. Most of the mass of these elements is soil-derived.

(3) Cl has a high enrichment factor, a strong seasonal variation with the lowest concentrations in the summer, the highest concentrations in the buffer sector, most of the mass in the coarse particle mode and dominating wet deposition. The main part of this

element originates probably from seaspray with the Atlantic as the major source and with some contribution from the Baltic.

(4) K has a quite high enrichment factor in the fine particle mode, an unusually broad size distribution, a small seasonal concentration variation and dominating wet deposition. We are presently not prepared to suggest the most important source or combination of sources for this component, but soil and seaspray are two of the possible contributors.

Cr and Br are based on rather incomplete data but would tentatively be placed in groups 1 and 3, respectively.

Acknowledgements—We are very much indebted to Lennart Persson at Sjöängen who operated the sampling equipment. The authors are grateful to K. R. Akselsson and J. W. Winchester for valuable comments on the manuscript. This work was supported by the National (Swedish) Environment Protection Board.

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APPENDIX

In a log-normal distribution the median (M) and the geometric mean (G) should coincide and the arithmetic mean (A) can be derived from $A = M \cdot \exp(\sigma_g^2/2)$ where σ_g is the geometric standard deviation. In the figure it can be seen that M and G often are very close. The arithmetic mean is often a factor of 2 higher than M which according to the equation above gives $\sigma_g = 1.2$. However the calculated σ_g 's are between 2 and 3. This indicates a skew log-normal distribution for some of the elements. In some cases this can be explained as "disturbances" from the detection limit.



Fig. A.1. The frequency distribution of elemental concentrations for the fine (f) and coarse (c) particle size intervals (< 1 and $1-8 \mu\text{m}$ aerodynamic diameter). The numbers displayed are actual concentrations and the number of cases in each concentration interval. Also indicated are the arithmetic (A) and the geometric (G) means and the median (M).

Interelement and multi-station concentration evidence for large scale aerosol sulfur transport across Sweden

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(Manuscript received May 21, 1979 in final form March 3, 1980)

ABSTRACT

The concentrations of sulfur and several more elements were measured in a network of six sites in southern Sweden. High time resolution samples were taken using a continuous filter sampler and analysed by particle induced X-ray emission (PIXE). Simultaneous increases in the sulfur concentrations were seen along the network due to the inflow of polluted air masses. High sulfur concentrations generally occurred during south-westerly to easterly air flow. Some of the episodes, distinguished by their shorter duration and their elevated vanadium and nickel concentrations, are suggested to be of local origin.

1. Introduction

Interest in the possible long range transport of air pollution over distances greater than 1000 km has focused on sulfur in the form of gaseous SO₂, sulfuric acid and sulfates (Sweden's case study 1971, Rodhe et al., 1972; Brosset 1973). In the OECD study on long range transport of air pollutants (OECD, 1977), an estimate of a European budget for the total deposition of sulfur in 1974 has been made. The results show that large amounts of sulfur pollutants are transported over long distances under certain meteorological conditions. Furthermore, countries like Finland, Norway and Sweden receive considerably larger amounts of air pollution from abroad than are emitted within these countries (Ottar, 1977).

A comparison of chemical and meteorological data ideally should be made using aerosol sulfur concentration measurements with a time resolution comparable to the time variations in air flow pathways. The frequently employed strategy of sampling suspended particulate matter for 24-h periods often averages concentrations over different meteorological conditions of possible importance to pollution transport. Consequently, a time

resolution of less than 24 h for aerosol sampling may be a desirable improvement. The present investigation was undertaken as a field test of such a strategy.

It is important to distinguish between contributions from nearby pollution sources and the larger scale transport of pollutants from more distant sources. A short time resolution, such as employed in this study, may permit the identification of periods when concentrations are influenced by plumes from local air pollution emissions. A complete investigation of air pollution sulfur transport, of course, should include measurements of both gaseous and particulate forms of sulfur. In this investigation, however, only the aerosol was sampled for elemental analysis.

2. Experimental

Six sampling sites in southern Sweden were chosen for this investigation. These sites, with locations shown on the map (Fig. 1), are among those chosen for the precipitation sampling network operated by the International Meteorological

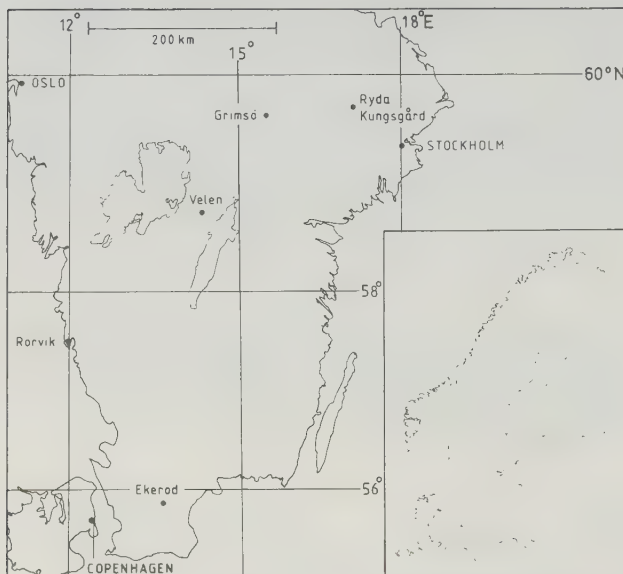


Fig. 1. Map showing six aerosol sampling locations in Sweden at Stockholm, Ryda Kungsgård, Grimsö, Velen, Rörvik and Ekeröd.

Institute in Stockholm (IMI-network) and are fully described elsewhere (Granat et al., 1977).

The sampling was generally carried out several meters above ground, at locations with negligible obstructions in the neighborhood. The samplers used were of a special continuous time sequence design (Nelson et al., 1976). These "streaker" samplers consist of an orifice which moves with a constant speed along a Nuclepore filter strip. Air is drawn through the orifice at a rate of 0.8 l/min. Hereby a 5-mm-wide streak of aerosol deposit is left on the filter. Consecutive 2-mm spots of the streak are analysed, resulting in a time resolution of approximately 2.4 h of sampling time. The uncertainty in the absolute time determinations of single spots are less than ± 1 spot = 2.4 h.

Particle induced X-ray emission, PIXE (Johansson et al., 1975; Johansson & Johansson, 1976), has been used for the multi-elemental

analysis of the streaker filter samples for sulfur and other elements ranging in atomic number from silicon to lead. In this investigation the elements Si, Cl, K, Ca and Fe in addition to sulfur, were usually seen above their detection limits in the samples. The analysis was performed by placing a filter strip, representing 8 days of sampling time on a single strip, into a vacuum chamber of the Van de Graaff accelerator at Florida State University and analysing successive steps by detecting X-rays generated during bombardment by 5 MeV protons. The X-ray spectrum from each analysis was recorded electronically during the approximately 1 min of proton bombardment time per step and later resolved into elemental constituents by computer procedures (Kaufmann et al., 1977).

The quality of the PIXE analysis is ensured by analysing standards during each accelerator run. Aerosol samples have been analysed repeatedly

revealing no changes in the composition of the elements reported here. However, recent data (Hansen et al., 1980) points out that in pre-concentrated samples losses of volatile sulfur species and losses induced by the proton irradiation can occur. These effects seem to be most serious for some sulfites. Atmospheric aerosol samples collected at a remote location on Nuclepore filters and analysed by PIXE have been compared with samples collected simultaneously on Acropore filters and analysed by the Thorin method at the Department of Meteorology, University of Stockholm. The results show an agreement between elemental sulfur from the PIXE-analysis and sulfate analysed wet chemically within $\pm 10\%$ in 75% of the samples (within $\pm 5\%$ in 50% of the samples). Since the X-rays emitted from sulfur atoms are relatively soft, self-absorption problems have to be considered. In this study the maximum aerosol deposit on the filter was 0.1 mg/cm^2 causing a negligible self-absorption of sulfur X-rays (Johansson et al., 1975). Large aerosol particles can also cause self absorption losses, e.g. for a $5\text{-}\mu\text{m}$ diameter particle the self-absorption would be approximately 5%. The pollution-derived sulfur-containing particles are found in the accumulation mode with a mass median diameter of $0.2\text{--}0.4 \mu\text{m}$ (Whitby, 1978). This implies that except for sea spray-derived sulfur-containing particles (larger than $2 \mu\text{m}$) no absorption effects can be expected. The detection limit for sulfur was set primarily by the thickness and composition of the filter material and averaged about 150 ng/m^3 . Since concentrations observed in this study ranged from several hundred to several thousand ng/m^3 ; sulfur was detected in all samples. However, certain other elements of interest, including vanadium and nickel, were only occasionally found above their detection limits.

The high sensitivity of the PIXE method in combination with the small sample requirements makes this method useful for the analyses of many types of samples. Since only a small sample ($\sim 10 \mu\text{g}$) needs to be collected, light weight and portable sampling devices may be employed, requiring small vacuum pumps with modest electrical power requirements. Depending on the information needed, different combinations of time, particle size and site-to-site distance resolution can be used. In a standard type 12–24 h aerosol sample (total filter or cascade impactor), 10–20 elements heavier than

phosphorus can be resolved in a 1–3 min routine analysis. On the sacrifice of a few elements and size distribution information, a time resolution of a few hours can be achieved. A streaker sampler can operate in rural or remote air with time resolutions from 2 to several hours. Since each streaker filter will contain samples collected over a week or more, its infrequent changing makes this sampler very easy and inexpensive to operate. The streaker sampler with a suitable time resolution, used in conjunction with PIXE analysis, is therefore ideal in many respects for use in air pollution sampling networks.

3. Results

Two sampling periods, each of 8 days' duration, in the spring of 1978, were selected for this study. The meteorological conditions included airflow from both northerly and southerly directions and therefore provided an opportunity to compare the composition of air passing over strong pollution source regions with that from less polluted areas. Fig. 2 shows 96 h back trajectories for air masses at the 850 mbar level, calculated by the Norwegian Meteorological Institute. Surface weather maps from the Swedish Meteorological and Hydrological Institute are shown in Fig. 3. The significance of the weather data is discussed further below in connection with the sulfur concentration data. In Fig. 4 the measured concentrations of aerosol sulfur are shown on a linear scale as a function of time of sampling. In all cases the concentrations varied markedly with time over a total range of up to a factor of 10, with large variations taking place frequently over a few hours. As the following discussion will make clear, some of the high sulfur concentration episodes may be due to local air pollution passing over the sampling sites, whereas other episodes appear to be large scale effects apparently due to sulfur transported over long distances.

One indication of the presence of a local sulfur plume (resulting mainly from the combustion of fuel oil) can be found by examining relationships between sulfur and other trace elements emitted from the same type of sources. Fuel oil often contains vanadium and nickel. The concentrations vary somewhat depending on the origin of the oil. The sulfur emissions are initially mainly in the form

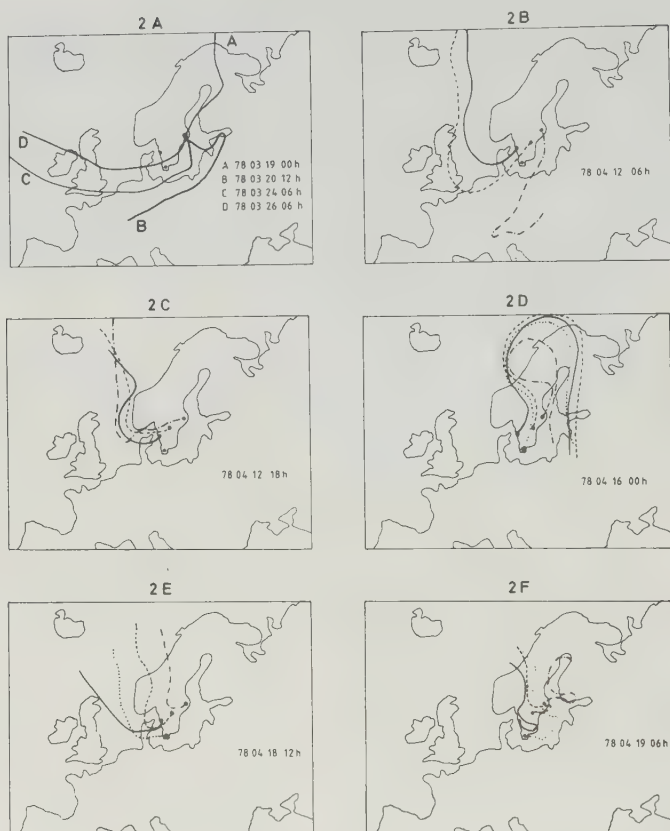


Fig. 2. A–I. Selected (representative) 96-h air mass trajectories at the 850 mbar level. The numbers indicate year, month, day and hour.

of sulfur dioxide gas which is gradually converted to sulfates at a rate depending, e.g. on the pollution level, and typically in the range of 0.1 to 10% per hour (Boulard et al., 1978; Calvert et al., 1978; Harrison et al., 1975). Vanadium and nickel are

already at the point of emission in particulate form. Unpublished data from a study undertaken by Lannefors and Hansson in the middle of Sweden, show that sulfur, vanadium and nickel have almost identical particle size distributions with almost all

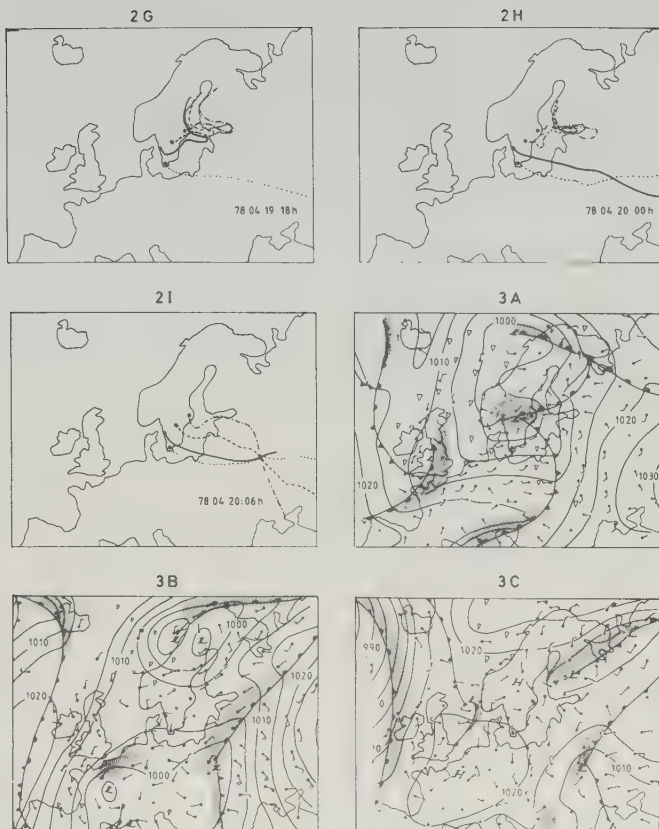


Fig. 3. A-C. Surface weather maps at 0600Z on April 12, 14 and 19, 1978.

the concentration in the accumulation mode. These results are in agreement with those of Charlson et al. (1978) stating coexistence of vanadium, nickel and sulfates on particles in the accumulation mode. Evidently these elements exist on particles having

the same size distribution and maybe also on the same particles. This implies that the sulfate deposition velocity should not differ very much from that of vanadium and nickel. However, since sulfur dioxide is gradually converted to sulfate

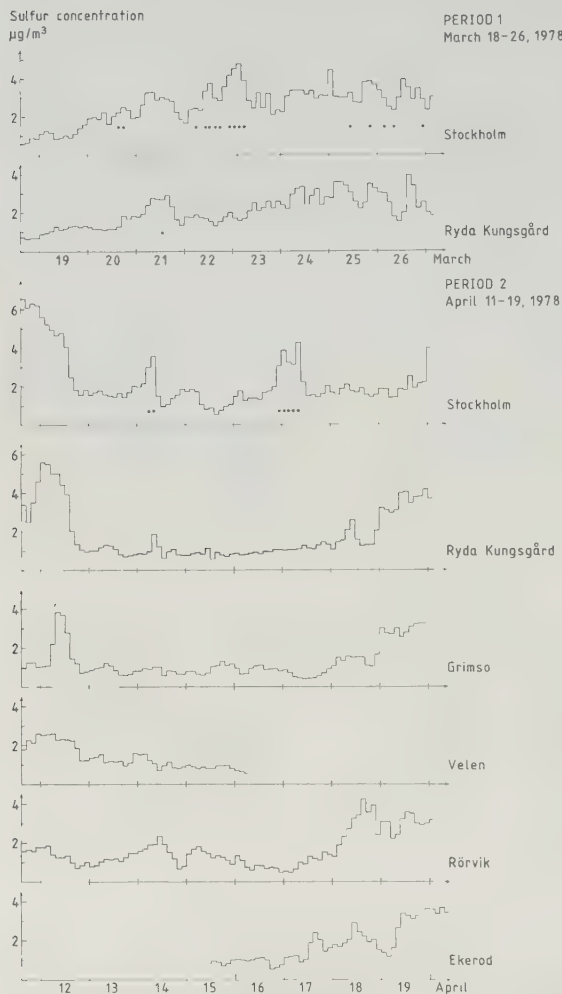


Fig. 4. Time variations of aerosol sulfur concentrations measured every 2.4 h at two sampling sites, March 18–26 and at six sampling sites, April 11–19, 1978. Periods of high V ($>100 \text{ ng}/\text{m}^3$) and Ni concentrations ($>60 \text{ ng}/\text{m}^3$) are indicated by dots (●) for V and circles (○) for Ni.

during the atmospheric transport, the ratio of sulfur to vanadium (or nickel) should increase with the transport distance.

Another indication of influences from local sources is the existence of nonsimilar concentration patterns at different sampling locations.

The Stockholm site and also the nearby Ryda Kungsgård site exhibited short-term sulfur concentration maxima during which significantly increased concentrations of nickel and vanadium were observed. At Stockholm, three pronounced episodes, March 22–23, April 13–14, and April 16–17 1978, were seen during which a correlation of sulfur with vanadium and nickel was found. One of these episodes is illustrated in Fig. 5. Sulfur concentrations reached their highest values during the night and early morning of the April 16–17 episode, when vanadium and nickel also were found substantially above their detection limits. From these results, and by examination of the time

variations at the Stockholm site, it appears that a substantial part of the total observed sulfur concentration during these episodes may be attributed to local plume sources.

Precipitation occurred during several of the sampling days and mostly during March. However, during the 12-h periods when precipitation was recorded, only minor amounts fell (i.e. less than 5 mm and usually also less than 1 mm in 12 h); probably causing only small effects on single elemental concentrations by aerosol particle scavenging. The conclusions made in this study are therefore probably not biased because of effects caused by precipitation.

Because of the frequent use of 24-h sampling routines, it is of interest to calculate from our results the 24-h average sulfur concentration seen on each of the sampling days. These are shown in Table 1 for the six sampling locations. The lowest average sulfur is less than 600 ng/m³ (equivalent to less than 1800 ng/m³ sulfate) and the highest is over 3000 ng/m³ (equivalent to over 9000 ng/m³ sulfate). Individual 2.4 h sulfur concentrations, however, reach as high as 6000 ng/m³ and as low as 400 ng/m³. Therefore, by smoothing over short time fluctuations, the 24-h averages exhibit less variability than is observed over shorter intervals, and episodes when local plumes contributed to the measured concentration may not be recognized.

4. Discussion

By comparing the air mass trajectories an attempt can be made to interpret the observed aerosol sulfur concentrations in terms of atmospheric transport from source regions. In Fig. 4 a striking resemblance is seen in many of the features of the time variability patterns at the different sampling stations in both the March and April periods. Except for the vanadium-related sulfur maxima seen in Stockholm (and also less distinctly at Ryda Kungsgård), the different sites show similarities. In the March 18–26 period at Stockholm and Ryda Kungsgård, concentrations are initially low and later relatively high. According to the air mass trajectories a generally north to northeasterly air flow persisted until noon March 20. A representative trajectory for this period is shown in Fig. 2A. On March 20 and 21 the air masses originated in the northern part of the European Continent and the western part of the

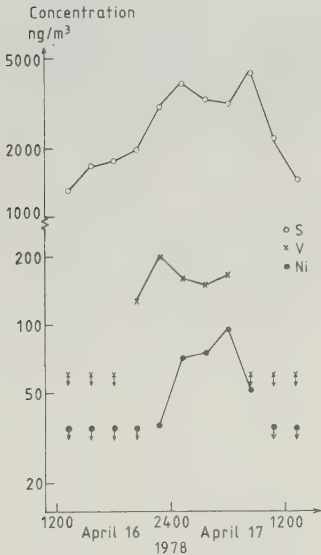


Fig. 5. Concentrations of sulfur, vanadium, and nickel observed at the Stockholm site on April 16–17, 1978. Detection limits are denoted by an arrow.

Table 1. 24-h mean sulfur concentrations, ng/m^{3a}

Date, March 1978								
Site	19	20	21	22	23	24	25	26
Stockholm	1050	2080	2720	2970	3180	3110	3350	3080
Ryda Kungsgård	1170	1360	2240	1700	2140	2790	3050	2610
Date, April 1978								
Site	12	13	14	15	16	17	18	19
Stockholm	3690	1630	1890	1120	1690	2470	1700	1890
Ryda Kungsgård	3490	986	988	808	896	1160	1613	3560
Grimsö	1870	849	811	912	874	588	1390	2970
Velen	2110	1260	1070	881				
Rörvik	1240	1150	1560	1370	796	1010	2910	3020
Ekeröd				869†	914	1490	2060	2730

* Arithmetic means of 10 observations per 24 h. Sulfate equivalent = $3 \times$ sulfur concentration.

† Based on only six observations

(see Fig. 2A). Higher sulfur concentrations (not related to vanadium and nickel) occurred during these days. Late March 21 the air flow again became north to northeasterly and the sulfur concentrations decreased. A local episode can be discerned in Stockholm on March 22–23. On March 23 the air flow changed to a south to southwesterly direction passing in over the British Isles and the northern part of the European continent (see Fig. 2A). The same flow persists throughout the first sampling period with only minor direction changes in the trajectories. Concentrations of sulfur were generally high but variable. The variations which can be seen at both locations can be accounted for by minor changes in the track of the air masses, sometimes passing in over the northern part of the European continent, sometimes passing over the North Sea (see Fig. 2A). Influences from local sources as well as precipitation scavenging can also help to explain these variations. The results above suggest that southerly flow is associated with higher sulfur concentrations (not related to vanadium and nickel) on a regional scale.

In the April 11–19 sampling period, observations were made at all six sites except for some electrical malfunctions during the first 3 days of sampling in Ekeröd and the last 3 days in Velen. As can be seen from a surface weather map (Fig. 3A) the weather situation on April 12 was dominated

by a circulation around a low pressure center in the middle of Sweden. This created a general inflow of air masses from the Norwegian Sea at the Rörvik sampling site. At the Stockholm, Ryda Kungsgård, Grimsö and Velen sites air masses that had passed over the European continent came in from south to the southwest (see Fig. 2B). As a result increased sulfur levels were seen at the latter sites (especially in Stockholm and Ryda Kungsgård), while the sulfur concentration at Rörvik remained low (see Fig. 4). Late April 12 the air flow changed somewhat not passing over the European continent or the British Isles (see Fig. 2C). This air flow remained until April 18 except for a period on April 15 and 16. During April 15 a flow around a low pressure center situated in northern Scandinavia developed, bringing up old continental air masses to the sampling network (see Fig. 2D). However, no effects can be seen on the sulfur concentrations. During the period April 13 to 18 (including April 15 and 16) the sulfur levels were low except for the two local episodes seen in Stockholm on April 13–14 and April 16–17. The weather maps for April 14 and 17, shown in Fig. 3B and 3C indicate very light winds and clear skies in the Stockholm area, thus reducing mixing and increasing the stability. These conditions are favourable for trapping local emissions, which can be seen as increased sulfur concentrations (related to V and Ni) during the night and morning of April 13–14

and April 16–17. When the first local (V-related) Stockholm episode is broken up, increased sulfur concentrations can be traced at the Ryda Kungsgård site.

On April 18 a complicated flow pattern started to develop. This included first a weak flow from northwest to west (see Fig. 2E) and then during April 19 an even weaker flow mainly from the north but taking different nonstraight paths to the sampling sites (see Fig. 2F). High sulfur concentrations were seen in Rörvik and Ekeröd and could also be traced at Grimsö and Ryda Kungsgård on April 18. Even higher sulfur concentrations (see Fig. 4) were found all over the network on April 19. The weak flow in combination with passages over source areas in Denmark and southern Sweden are possible explanations for those high sulfur concentrations. The accuracy of the calculated air mass trajectories could also be questioned during a complicated meteorological situation.

However, late April 19 and April 20 the situation straightened out and the flow was gradually altering to an easterly flow (see Fig. 2G, 2H and 2I), and the sulfur concentration level became high all over the network (see Fig. 4).

5. Conclusions

This comparison of sulfur concentrations obtained at simultaneously operated sampling sites suggests that large scale features seen in the time variation of the sulfur concentration are the result of long-range transport into Sweden of polluted air masses from a generally southwest to easterly

direction. Superimposed upon this are local emission effects (seen in Stockholm and Ryda Kungsgård), showing vanadium and nickel associations with sulfur, which may be attributed to sources in the Stockholm area. This study illustrates the advantage of combining a network of sampling sites with comparably high time resolution samplers (0.1 day). Good time resolution and multielement analysis are needed in order to discern local episodes of short duration. Such a time resolution is also needed to study the flow patterns of the air masses at nearby stations. For long-range transport studies with the sampling sites located far apart, with no local sources, a time resolution of 12–24 h appears to be sufficient. Cascade impactors can thus be used, permitting a size classification of the aerosol (Johansson et al., 1976; Lannefors et al., 1977). In combination with multielement analysis such as PIXE analysis, important information on possible pollution and natural sources can be obtained.

6. Acknowledgements

Generous assistance was offered by several individuals at the sampling sites, which is gratefully acknowledged. This work was supported in part by the Swedish Society for the Conservation of Nature for aerosol composition measurements over southern Sweden, by the U.S. Environmental Protection Agency for Mesoscale Sulfur Balance Studies, and by the Swedish National Environmental Protection Agency for travel for one of us (H.L.) to Florida State University to complete this study.

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КРУПНОМАСШТАБНЫЙ ПЕРЕНОС СЕРНЫХ АЭРОЗОЛЕЙ ЧЕРЕЗ ШВЕДИЮ ПО ДАННЫМ ИЗМЕРЕНИЙ КОНЦЕНТРАЦИЙ РЯДА ЭЛЕМЕНТОВ НА СЕТИ СТАНЦИЙ

На сети из шести станций в Южной Швеции измерялись концентрации серы и нескольких других элементов. Пробы с высоким разрешением по времени брались с использованием непрерывного фильтрового заборника и анализировались с помощью рентгеновской эмиссии, возбуждаемой частицами. Последовательные увеличения в кон-

центрации серы наблюдались на сети станций при притоке загрязненных масс воздуха. Высокие концентрации серы обычно встречались при ветрах с юго-запада до востока. Локальные выбросы серы различались их более короткой длительностью и связью с повышенными концентрациями ванадия и никеля.

LONG RANGE AEROSOL TRANSPORT IN SOUTHERN SWEDEN: AN EXAMPLE OF
MULTIVARIATE STATISTICAL EVALUATION METHODOLOGY.

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ABSTRACT

The utilization of multivariate statistical techniques, with emphasis on the rather new method SIMCA, when applied to multielemental data is discussed. The procedures of scaling and normalizing are described. The data base used is from a project studying long range aerosol transport to southern Sweden. SIMCA reveals low variability in fine mode elemental composition in southerly air masses being clearly different from the elemental compositions found in northerly air masses.

INTRODUCTION

Multivariate statistical techniques have been applied to air pollution data with some success during the last decade. The most widely used methods are principal component and factor analysis while in some cases cluster analysis has been used. These techniques have mostly been used in an explorative hypothesis generating way in order to find correlating parameters in the data base studied, e.g. source patterns (1,2).

Factor and principal component analysis combined with other statistical techniques have been used in attempts to achieve more quantitative results. Henry and Hidy (3) have used multiple linear regression between a dependent variable and the principal components obtained by analysis of a set of other variables. Another interesting method is target transformation factor analysis (4). This method is aimed at quantifying pollution sources. The factor rotation usually done after the factor analysis is steered in the sense that the resulting factors should, as closely as possible, resemble any one of a set of test vectors. These preliminary factors have a source characteristic elemental composition that could be altered during the iterative rotation procedure to achieve the best possible agreement. One problem with this method is that the solutions obtained are not unique.

This work utilizes a recently developed multivariate statistical program package named SIMCA (5), which combines a pattern recognition technique and principal component analysis. The aim is to demonstrate how this multivariate technique can be applied to multi-elemental data i.e. a typical PIXE data set. Important procedures like normalization with respect to meteorological influence and scaling are discussed.

A more detailed evaluation of the data set is presented in (6).

EXPERIMENTAL

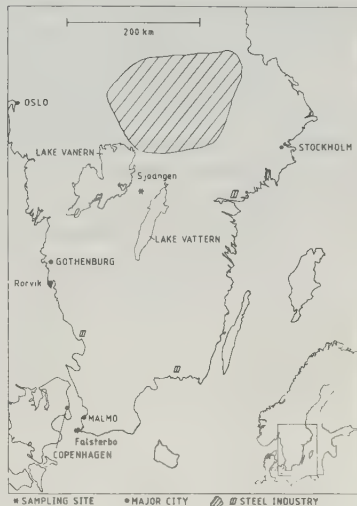
Sampling and analysis

The sampling sites Rörvik and Falsterbo (see fig. 1) were chosen to represent locally undisturbed, westerly and southerly aerosol transport to southern Sweden. In addition a third site, Sjöängen, was used as a relatively undisturbed background inland reference site.

The Falsterbo sampling site is located on a peninsula on the very southwestern edge of southern Sweden. Nearest larger industrial areas are found in

Copenhagen (1 million inhabitants) 30 km to the north-west and Malmö (1/4 million inhabitants) 25 km to the north-east. The Rörvik sampling site is operated by the Swedish Water and Air Pollution Research Laboratory and is situated on a peninsula 30 km south of Gothenburg (1/2 million inhabitants). The Sjöängen sampling site is located between Lake Vänern and Lake Vättern 200 km north-east of Gothenburg.

FIGURE 1. Map showing the location of the sampling sites (Falsterbo, Rörvik and Sjöängen), some major cities and the Swedish steel industry locations. (The area contains several industries.)



The study consisted of approximately 6 months of sampling according to a fixed schedule, since no pre-warning of long range transport episodes could be obtained. Based on meteorological information, i.e. back trajectories calculated by the Norwegian Meteorological Institute and synoptic weather charts issued by the Swedish Meteorological and Hydrological Institute, a selection was made of samples representing meteorological situations where air masses having well defined and non complicated transport paths, i.e. representing well developed high or low pressure weather conditions. In this way about 20 samples taken simultaneously at each of the three sampling sites and an additional 5 samples taken simultaneously at each of the Falsterbo and Rörvik sampling sites were selected for analysis. The sampling time was 24 hours from 0700 GMT.

The samplers, Battelle-type single orifice cascade impactors (7), fractionate the aerosol particles into five logarithmically equidistant and two open ($< 0.25 \mu\text{m}$ and $> 8 \mu\text{m}$ aerodynamic diameter) particle size intervals. The first stage ($> 8 \mu\text{m}$) is only used to give a rather well defined upper cut-off (8), since the large particle sampling efficiency is wind speed dependent.

Analysis for elements from sulphur and heavier was undertaken by particle induced X-ray emission (PIXE) (9). Typically 10-15 elements were detected.

The total uncertainty resulting from sampling and analysis is estimated to be of the order of 25 % (8) while inter-element comparisons in the same sample will result in considerably lower uncertainty, in most cases less than 10%.

Data classification

The importance of long range transport from continental Europe and Great Britain can be studied by combining meteorological data and aerosol composition data. The samples (sampling days) were classified into sector North, South or East according to the air mass history (fig. 2), using 850 mbar isobaric back trajectories.

Sector North is limited to areas where no larger source areas exist while sector South contains the main part of the large source areas in Europe. Between sectors North and South and South and East, buffer sectors were placed in order to reduce the risk of erroneous classification of samples with respect to the uncertainty in the trajectory calculations. Samples having air mass trajectories within these sectors were therefore not included in the evaluation.

MULTIVARIATE STATISTICAL EVALUATION

The concentration of several atmospheric aerosol components can be expected to be correlated due to mutual sources. The interpretation could therefore be more precise if this correlation is used in a multivariate statistical evaluation, rather than in a univariate, taking all measured variables into simultaneous consideration. A problem that has to be considered in both univariate and multivariate analysis is that the measured variables are dependent on more or less unknown meteorological variables. The individual elemental concentrations in urban locations are correlated to about 50% because of the dominating influence of the meteorological factors on the data set (10). It can be expected that this influence is even greater when considering aerosol long range transport.

The multivariate statistical methods most frequently applied to atmospheric chemistry data do not allow validation of a suggested hypothesis but rather generate a hypothesis. Common for all the multivariate statistical techniques is that the M measured variables define a space, measurement space or M-space, where each variable has its own axis. Factor and principal component analysis (see e.g. (11)) are widely used multivariate statistical methods which can be described in short as techniques to find independent factors consisting of

correlated variables. These factors can be used to span the measurement space. As the number of factors is often much fewer than the number of variables, the inherent structure of the data set is more easily understood. However, if the distribution of the data points in the M-space is inhomogeneous, these methods will be less efficient in describing the covariation patterns (12). A method of investigating the homogeneity of the data distribution is obviously needed. Cluster analysis can be used for this task with some success (13). A difficulty with this method is that the results obtained sometimes are hard to interpret (14). A rather new multivariate statistical method, SIMCA (5), treats the homogeneity problem in another way. Data believed to form clusters are thus divided into different classes which are fitted to separate models by principal component analysis of the data in each class. The residuals are calculated for each object believed to belong to a certain class which are used to determine confidence intervals for the models. In this way quantitative statistical measures are obtained on:

- (1) each model's ability to describe its class
- (2) the homogeneity of the data distribution in each class
- (3) the significance of the class separation
- (4) the importance of the different variables in defining the models
- (5) the importance of the different variables in discriminating between the classes.

Data-set inspection

In the statistical evaluation of a data set it is essential to eliminate disturbing influences on the material. During the evaluation strong indications of a local Cu contamination in Falsterbo have been found. Furthermore strong evidence, see e.g. (15), points to considerable Cl losses from aerosol samples under conditions of low pH. In this data set Cl shows very little covariation with other potential sea-spray variables such as S, K and Ca, and also with any other of the variables measured. Therefore very little information about these elements is provided by Cl. Based on these observations Cl and Cu have been excluded from the analysis.

Principal component analysis over the whole data set indicates that there are samples deviating in the elemental composition in the broad sector South. Among the samples in air masses originating in the most westerly part of sector South (west of the English Channel, see fig. 2) outliers can occur. These samples form, together with one occasion when all three sampling sites received air masses that had passed over England and Central Europe, a group of south

westerly samples which will not take part in the modelling of sector South. This group of samples, together with the sector East samples, will instead be used as a test set, i.e. these samples will be tested with respect to which class they belong to. The two most easterly air masses in sector South (east of central Poland) are also considered as potential outliers and were not included in the sector South modelling (fig. 2).

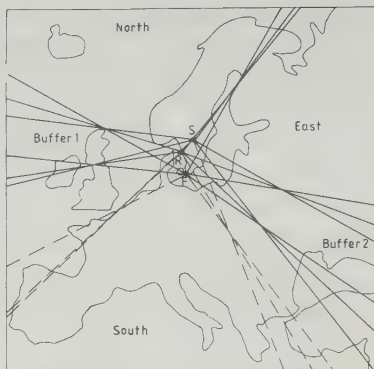


FIGURE 2. Sector classification

Scaling and Normalization

Unknown meteorological variables dominate the variability in the data set, which is illustrated by the correlation matrix. The correlation coefficient between the elements in this data set is in very many cases larger than 0.8, e.g. for Pb and Mn it is 0.9, which can probably not be explained by mutual sources. The meteorological influence can be reduced by normalizing to another variable which also depends on the meteorological situation but is as independent as possible of the aerosol source characteristics. A division by the aerosol mass in respective mode seems to be the best alternative for normalization. Since the total mass is not determined in the fine mode, the sum of all elements participating after an average scaling of each element, has been chosen. The normalization reduces the measurement space by one dimension. Before applying the multivariate statistical program the variance for each variable has been scaled to 1 which means that all the variables will have the same weight.

The alteration in the measurement space due to the normalization is illustrated in the plots of the first two principal components for a non-normalized and a normalized data set in figures 3a and 3b respectively. The first principal component in fig. 3a depends on all variables to almost the same extent (85% of the variance), reflecting the influence of meteorological variables. In figure 3b the variables split up on the different principal components in a totally different way, which will be discussed below. The structure of the data seem to be the following:

- (1) sector North samples have large variations in elemental composition.
- (2) sector South samples are closer together and located at the boundary of the sector North space.

(3) sector East samples are spread out but mostly located close to the sector South samples.

Can this structure be validated?

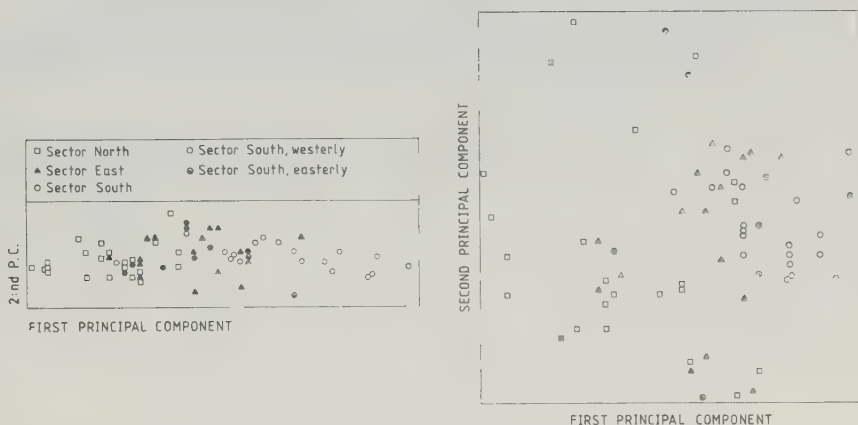


FIGURE 3. Measurement space projected on the plane spanned by the two factors that explains most variance (drawn to scale) a/ With variance scaling b/ With normalization followed by variance scaling.

SIMCA applied to the data set

There are indications of relative elemental composition differences in the fine particle mode (aerodynamic particle diameter $D_p < 2 \mu\text{m}$) between aerosol samples in different wind sectors. SIMCA is therefore applied to the data base to produce quantitative measures based on this indication. The first step in SIMCA is to form class models. This is done by principal component analysis. Expressed in formula the model is written

$$x_{ik} = \alpha_i + \sum_{a=1}^A \beta_{ia} \theta_{ak} + \epsilon_{ik}$$

i = index of the variable
 k = index of sampling occasion
 x = data
 α = coordinate for class centre in element space
 β = principal component
 θ = coefficient
 ϵ = residual
 A = dimension of class model
 q

When forming the models, the variance for each element in each class is scaled to 1, in order to make the principal components of each class dependent only on its own measurements. The dimensions of the classes are determined by cross-validation (16). In this case both A_{North} and A_{South} are 3.

The residual standard deviation for the objects applied to their own class model is expressed as:

$$S_0 = \left(\sum_{i=1}^M \sum_{k=1}^{N_q} \varepsilon_{ik}^2 ((m-A_q)(N_q-A_q-1))^{-1} \right)^{0.5}$$

M = number of variables
 N_q = number of objects in class q
 m = dimension of measurement space
 (in our case $m=M-1$)

The distance from a point to a class model in which the point has not been used to shape the model is:

$$S_p^{(q)} = \left(\sum_{i=1}^M \varepsilon_{ip}^2 (m-A_q)^{-1} \right)^{0.5}$$

An F-test is performed to calculate the probability that a point belongs to a certain class q . For

$$\text{for } F((m-A_q), 0.5(m-A_q)(N_q-A_q-1))$$

the probability levels of 1% and 5% for a data point to belong to a certain class are calculated by:

$$S_p^{(q)} = F_q S_0^{(q)}$$

In fig. 4a the S_p -values for sector North and the reduced sector South are plotted for both models. The probability levels of 1% and 5% for a data point to belong to a certain class (obtained by the F-test) are indicated. This figure shows that the sector North measurements (except one) have an elemental composition that does not fit the sector South model. It can also be seen that the variation in elemental composition for sector North measurements is such that when forming a model for these measurements, the remaining data points are equally well described. From the distribution of the test set in fig. 4a it is found that the sector "South, westerly" measurements in all except one case are close or rather close to the sector South class model, while the sector "South, easterly" measurements do not fit the model. The sector East measurements can not be separated from any of the two class models.

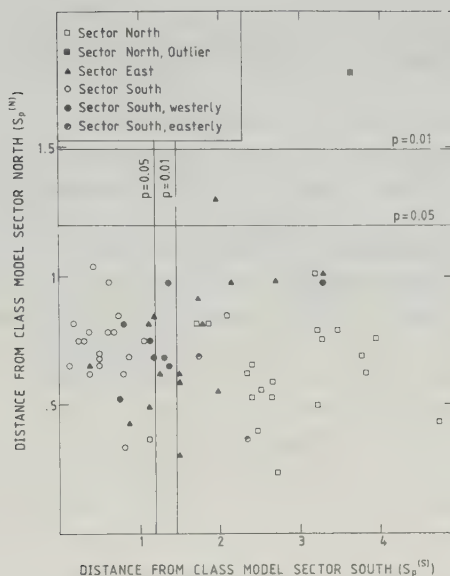


FIGURE 4. a/ The objects (sampling occasions) fit to sector South and sector North class models.

The distance between two classes r and q is expressed:

$$d_{r,q} = ((S_q^{(r)})^2 + S_r^{(q)})^2 (S_0^{(r)} + S_0^{(q)} - 1)^{-1})^{0.5}$$

$$\text{where } S_q^{(r)} = \left(\sum_{i=1}^M \sum_{p=1}^N e_{ip}^{(q)} \right)^2 ((M - A_r) N_q)^{-1})^{0.5}$$

is the residual standard deviation for the objects of class q when applied to the model of class r .

$d_{r,q}^2$ is approximately F-distributed (17) as:

$$F(0.5((N_r - A_q)(m - A_q) + (N_q - A_r)(m - A_r)), 0.5((N_r - A_r - 1)(m - A_r) + (N_q - A_q - 1)(m - A_q)))$$

The distance between the class models North and South is 3.8. This figure can be compared with the distance obtained for equal classes on the 1% level of probability, $(F_{0.01})^{0.5} = 1.2$, i.e. the classes are very well separated. Thus,

it can be concluded that there are significant differences in elemental composition when comparing air masses originating in central Europe with northerly ones.

The variables discriminating between two classes can be calculated by the SIMCA routine PLS (partial least squares modelling with latent variables) (18). In principle this is done by adding an extra variable. The added variable was given a certain value for all samples belonging to one class and a different value for all objects belonging to the other class. In this way the added variable expresses class belonging. This kind of problem is a pseudo inverse solution of the canonical variate problem (19). The PLS routine then calculates the combinations of the other variables that explain the variance in the added (dependent) variable, i.e. the interclass discrimination properties of the variables.

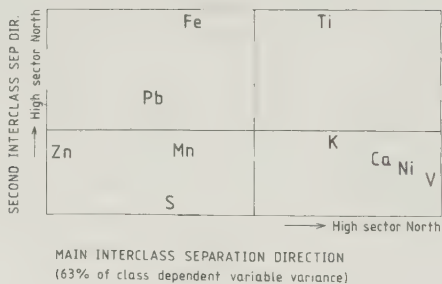


FIGURE 4. b/ The variables' importance in discriminating between the classes for sector South and North.

In figure 4b the first two components that describe the differences in elemental composition between sectors North and South are shown. The main interclass separation direction explains 63% of the dependent variable variance, while the second only explains a few percent. The acceptance of the sector North model (see fig. 4) for sector South data points makes the separation pattern somewhat complicated. This pattern would be more distinct if both the classes were discriminating, see e.g. (6). The main elements which differ between the classes are Zn, V, Ni and Ca. The higher relative content of V and Ni - related Zn in northerly air masses is in good agreement with firstly the location of heavy metal emissions in Sweden, see fig. 1 and (20), secondly the heavy metal relative composition from the sources in Sweden compared with that in central Europe (21). (Source inventories are not available for Ca.) The separation pattern is also in accordance with results obtained by Martinsson et al. (6) where the foreign contributions in air masses originating in central Europe were

calculated to be about 50% for V and Ni and as high as around 90% for Zn, when passing over southern Sweden.

CONCLUSIONS

When applying a multivariate statistical technique to atmospheric aerosol data, mass normalization of the data reduces the covariation caused by meteorological factors and therefore results in better resolution of elemental concentration relations.

The multivariate statistical method SIMCA can be used in a hypothesis testing way in contradiction to more widely used multivariate statistical techniques (e.g. principal component analysis, factor analysis and cluster analysis) which generate hypotheses. In the light of this SIMCA constitutes a very useful tool for the determination of cluster separation, where routines for calculating the importance of the different variables in discriminating between the clusters also are provided.

In our application example it is found that the samples taken from air masses in southern Sweden originating in central Europe form a cluster significantly different from measurements in northerly air masses having a larger variability in the fine mode aerosol elemental composition between the samples.

It has been shown that SIMCA has great potential in the evaluation of atmospheric aerosol data such as those produced by PIXE analysis, because of its ability to recognize and test the significance of patterns in the data.

ACKNOWLEDGEMENTS

Sampling assistance at the three sampling sites is gratefully acknowledged. We are also very grateful to Dr S. Wold, the SIMCA creator, for introducing us to SIMCA and for his kind assistance during the data evaluation. Important comments on the manuscript were provided by prof. K.R. Akseleson. Valuable comments were also provided by Dr M. Hagnell. This work was partly supported by the National (Swedish) Environment Protection Board.

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SOUTHERN SCANDINAVIAN AEROSOL COMPOSITION AND ELEMENTAL SIZE DISTRIBUTION
CHARACTERISTICS DEPENDENT ON AIR-MASS HISTORY

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ABSTRACT

The influence of aerosol long range transport in southern Sweden was investigated from a data base consisting of simultaneous cascade impactor measurements at three sampling stations, two coastal and one inland rural location. The study focused on sulphur and heavy metals determined by particle induced x-ray emission (PIXE) analysis. The influence of local emissions was minimized by eliminating samples which were strongly suspected to be contaminated. These were identified through size distribution alterations in combination with the concentration levels obtained. Based on air mass back trajectories the samples were classified into either a southern, a northern or an eastern sector or into one of the buffer sectors located in between the sectors mentioned above. Sector South elemental concentrations were generally one order of magnitude higher than those of sector North, while intermediate concentrations were found in the easterly sector. Intercomparisons of simultaneous fine mode elemental concentration measurements classified into sectors South and North, respectively, provides a method for calculating the sector South foreign contribution of the elemental concentrations in southern Sweden. These calculations, not based on emission data, result in a foreign contribution of the order of 50 - 90% (lowest for components like V and Ni and highest for Ti, Mn and Zn) to the metal concentrations. The multivariate statistical method SIMCA revealed that the sector South aerosol elemental composition was dependent on particle size in the accumulation mode. Elements such as S and V (or Ni) normally assumed to originate mainly from the same sources (fossil fuel combustion) were clearly separated and instead S clustered with K, Mn and Zn. This indicates that the transformation processes are more important for the covariation of S with other elements than the source origin. Transformation of SO_2 in hygroscopic particles rich in K, Mn and Zn (compared with less hygroscopic particles rich in V and Ni) is a possible mechanism which would explain the results found.

INTRODUCTION

Aerosol long range transport has been the subject of great interest in research in recent years and is now a well established phenomenon (see e.g. Brosset 1980, Wolff 1980 and Ottar 1980). Sulphur, both in particulate form and its gaseous precursor, is by far the most studied component in long range transport. It has been shown that sulphur, in the form of sulphuric acid, is responsible for the main part of the acidification of lakes in Scandinavia (Acidification today and tomorrow, 1982). Calculations based on different measurements (OECD 1977, Högström 1977, Lannefors et al. 1983) indicate that roughly 75% of the sulphur deposition (concentration in Lannefors et al. 1983) in southern Sweden has a non-Swedish origin. Furthermore similar calculations for some heavy metals (V, Ni and Pb) by Lannefors et al. (1983), indicate that the contribution from non-Swedish sources is on the same level (25 - 75%) as that from Swedish sources.

This work is based on simultaneous measurements at three locations in southern Sweden. The length of the sampling periods (24 hours) permits meteorological interpretation on synoptic and larger scale. This is used to evaluate the continental European and British contribution to the measured aerosol composition at the different sampling sites relative to the Swedish contribution.

Multivariate statistical techniques have been applied to air pollution data with some success during the last decade. The most widely used methods are principal component and factor analysis while in some cases cluster analysis has been used (Gaarenstroom et al. 1977, Gatz 1978). Factor analysis with a modified factor rotation has also been introduced, so-called target transformation factor analysis (Hopke 1980). These techniques have mostly been used in an explorative hypothesis generating way in order to find correlating parameters in the data base studied, e.g. source patterns. The latter technique also provides a quantitative measure. This work utilizes the multivariate statistical program package SIMCA (Wold et al. 1981), which combines a pattern recognition technique and principal component analysis. SIMCA has earlier been applied to atmospheric aerosol data, see Hansson et al. (in press).

In this work different approaches are taken to characterize the aerosol long range transport with special emphasis on elemental composition and size distribution.

The sampling sites at Rörvik and Falsterbo (see fig. 1) were chosen to represent locally undisturbed, westerly and southerly aerosol transport to southern Sweden, respectively. In addition a third site, Sjöängen, was used as a relatively undisturbed inland background reference site.



FIGURE 1. Map showing the location of the sampling sites (Falsterbo, Rörvik and Sjöängen), some major cities and the Swedish steel industry locations. (The large area denotes several industries.)

The Falsterbo sampling site is located on a peninsula on the very south-western edge of southern Sweden. The local surroundings consist of sandy beaches, a golf course, and the sea within 0.5 km in westerly, southerly and easterly directions. The sampler was placed on top of a 25 m high lighthouse. The nearest larger industrial areas are found in Copenhagen (1 million inhabitants) 30 km to the north-west and Malmö (1/4 million inhabitants) 25 km to the north-east.

The Rörvik sampling site is operated by the Swedish Water and Air Pollution Research Laboratory and is situated on a peninsula 30 km south of Gothenburg (1/2 million inhabitants). The land surrounding the site consists of meadows and the seashore 0.5 km to the west. The sampler was placed on the roof of the one-storey sampling station approximately 4 m above the ground.

The Sjöängen sampling site is located 200 km north-east of Gothenburg

between Lake Vänern and Lake Vättern. The local surroundings consist of forested areas and the nearest large agricultural area is some 10 km to the south. The sampler was placed on top of a tower approximately 17 m above the ground in an area which was cleared of trees and covered with grass.

The sampling program comprised approximately 6 months of sampling according to a fixed schedule, since no warning of long range transport episodes could be obtained. Based on meteorological information i.e. 850 mbar isobaric back trajectories calculated by the Norwegian Meteorological Institute and synoptic weather charts issued by the Swedish Meteorological and Hydrological Institute, samples were selected which represented meteorological situations where air masses had well defined and uncomplicated transport paths (i.e. well developed cyclonic or anticyclonic weather conditions). In this way about 20 samples taken simultaneously at each of the three sampling sites and an additional 5 samples taken simultaneously at each of the Falsterbo and Rörvik sampling sites were selected for analysis. The sampling time was 24 hours starting in the morning at 0700 GMT.

The samplers, Battelle-type single orifice cascade impactors (Mitchell and Pilcher 1959), fractionate the aerosol particles into the following intervals: <0.25 , $0.25-0.5$, $0.5-1$, $1-2$, $2-4$, $4-8$ and >8 μm aerodynamic diameter. The <0.25 μm stage consists of a 0.4 μm Nuclepore membrane filter while the impaction stages have a paraffin greased polystyrene coating which is removed prior to analysis. The >8 μm stage is only used to give a rather well defined cut-off (Lannefors et al. 1983), since the largest particles are difficult to sample with a high and constant efficiency. The samplers were protected during sampling by a conical aluminum rain shield.

Analysis of elements heavier than phosphorous was undertaken by particle induced X-ray emission (PIXE) (Malmqvist et al. 1982). Typically 10-15 elements were detected in a 3-minute bombardment period (40 μC charge) using 2.55 MeV protons generated by the pelletron accelerator at the Department of Nuclear Physics, Lund Institute of Technology. The overall uncertainty from the sampling and analysis is estimated to be of the order of 25 % (Lannefors et al. 1983) which is low compared with the elemental concentration variations discussed here. Inter-element comparisons in the same sample will result in a considerably smaller uncertainty, in most cases less than 10%.

RESULTS AND DISCUSSION

The results presented are based on selected samples representing occasions with well developed meteorological conditions, some with possible aerosol long

range transport from large source areas. Therefore the data to be presented can not be interpreted as being representative of average or typical values. Annual mean concentrations and average non-Swedish aerosol composition influences are given in Lannefors et al. (1983) for the location Sjöängen, which was also used in this study.

LOCAL CONTAMINATION

Identifying the contribution from local sources is very difficult and complicated. We have basically relied on two assumptions to identify the most serious cases of fine particles local contamination:

- a/ The sampling stations are on most sampling occasions not exposed to local contamination. Therefore such events (if relevant) can be identified by unexpectedly high concentration levels for some elements.
- b/ The elemental size distributions for samples affected by local emissions (fresh combustion aerosol) should have a mass median diameter considerably smaller than non-affected samples (Whitby 1978).

The sampling sites were selected in such a way as to minimize local contamination. However, the sites at Falsterbo and Rörvik will run the risk of being influenced during northerly winds carrying emissions from Malmö/Copenhagen and Gothenburg, respectively. Such contamination was identified on one occasion in Falsterbo resulting in a large increase in the levels of V, Mn, Ni, Cu, Zn and Pb. Local and synoptic meteorological information pointed to Copenhagen as the only probable source heavily affecting the elemental concentrations of a north Atlantic air mass. This sample, deviating from the other samples in Falsterbo sector North, was excluded from the data base. No other samples were taken during similar wind conditions. High fine mode concentrations of copper were found during northerly trajectories at the Falsterbo site on 3 (out of 7) occasions which were possibly the result of local emissions. Therefore the copper concentrations for Falsterbo sector North are given with some reservation (table 1). On a few occasions local contamination from Gothenburg was suspected in Rörvik. However, this increased the average metal concentrations by less than a factor two.

Using this technique for the identification of a local contamination component and also remembering that local contamination is most probable during northerly winds lead to the conclusion that comparing air masses with northerly and southerly origin will rather underestimate than overestimate the importance of long range aerosol transport.

CONCENTRATION LEVEL DEPENDENCY ON AIR-MASS HISTORY

The importance of long range transport from continental Europe and Great Britain can be studied by combining meteorological data and aerosol composition data. The samples (sampling days) were classified into sectors according to their air-mass history (fig. 2). Sector North is limited to areas where no larger source areas exist while sector South contains the main part of the large

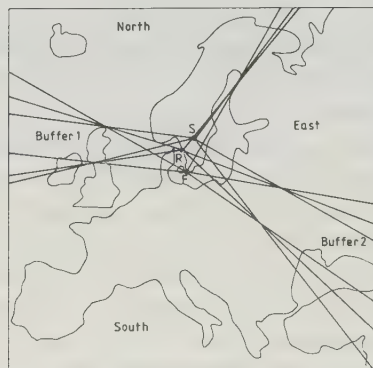


FIGURE 2. Sector classification of the samples with respect to air-mass history.

source areas in Europe. Buffer sectors were placed between sectors North and South and South and East in order to reduce the risk of erroneous classification of samples as a result of the uncertainty in the trajectory calculations. Samples having air mass trajectories within these sectors were not included since it is not clear what areas they have passed over on their way to the sampling sites. The major part of sector South trajectories were found between south-easterly and south-westerly directions which indicates that in this data set continental Europe is the main contributor in this sector. Few samples classified in sector East were collected, thus limiting the information from this sector. The main emphasis will therefore be on a comparison of results from sectors North and South.

In table 1 average elemental concentrations for southerly and northerly air masses for the three sampling sites are given. Also listed for comparison are values representing the eastern sector. Generally, the highest concentrations are found in sector South, sector East being intermediate and sector North lowest. Comparisons of fine mode (particles with an aerodynamic diameter $<2\mu\text{m}$) elemental concentrations in the northerly and southerly sectors are made for

TABLE 1. Average total ($<8 \mu\text{m}$ diameter) elemental concentrations (ng m^{-3}) in sectors South, North and East. The fine mode fraction (%), i.e. particles with an aerodynamic diameter less than $2 \mu\text{m}$, are given in brackets.

Site	FALSTERBO		RÖRVIK		SJÖÄNGEN		ALL SITES
Sector	South	North	South	North	South	North	East
No. samples	11	7	10	9	7	7	16
Element							
S	2000(92)	290(90)	1600(92)	190(74)	1400(96)	140(92)	800(93)
Cl*	170(9.6)	210(20)	110(13)	260(20)	37(30)	94(40)	57(37)
K	200(70)	41(63)	130(70)	45(38)	110(84)	25(77)	100(53)
Ca	270(41)	47(30)	180(29)	73(23)	66(58)	30(71)	180(20)
Ti	33(45)	3.8(50)	20(36)	7.8(33)	8.9(64)	2.0(70)	9.5(38)
V	7.3(85)	1.4(94)	4.8(84)	1.9(91)	5.4(93)	1.0(93)	3.0(94)
Cr	4.0(93)	1.1(92)	2.5(88)	1.5(92)	2.7(93)	2.5(92)	3.2(85)
Mn	20(83)	1.2(61)	12(77)	2.8(57)	11(89)	2.2(83)	5.4(65)
Fe	340(56)	39(54)	220(50)	69(36)	130(76)	21(70)	130(46)
Ni	3.4(88)	.89(79)	3.2(82)	1.7(90)	2.9(93)	.88(86)	2.4(88)
Cu	11(93)	3.7(97)+	5.5(86)	2.0(79)	3.5(92)	1.1(92)	3.2(84)
Zn	91(89)	4.5(82)	61(84)	5.2(88)	56(92)	6.2(91)	29(67)
Br	6.4(>91)	<2.1(-)	5.3(>89)	3.9(>85)	3.9(>85)	<2.1(-)	4.1(>85)
Pb	120(96)	14(96)	61(91)	14(88)	51(96)	5.9(88)	27(93)

+) suspected to be effected by local contamination.

*) possibly effected by losses (especially in the fine mode) due to the reaction with H^+ ions and subsequent evaporation of HCl (Heintzenberg et al. 1981).

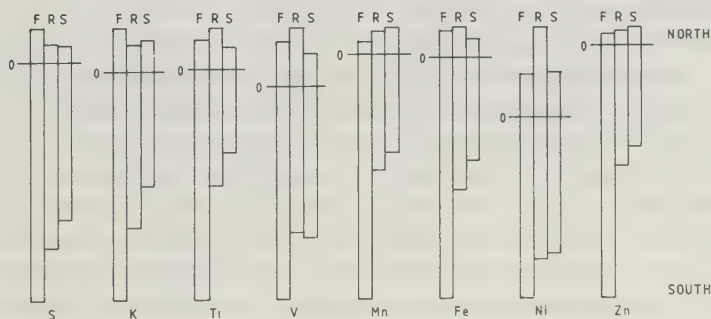


FIGURE 3. Relations between fine mode elemental concentrations at the different sampling sites (F=Falsterbo, R=Rörvik and S=Sjöängen) in sectors North and South. The concentrations are normalized to the sum of the highest sector North and sector South concentration for each element (linear scale).

some of the elements in figure 3. From table 1 it is clear that all elements except Cl exhibit higher concentrations in the southern sector. Furthermore S, Mn, Zn and Pb, especially their fine mode component, show the strongest directional dependence with, in most cases, a factor of ten higher concentrations in southerly compared with northerly air masses. It should also be noted that elements like K, Ca, Ti and Fe, normally connected with soil erosion, show a prominent directional dependence most pronounced in the fine mode, being typically a factor of 3-5 lower in sector North than in sector South. The observed directional dependence, very similar to that described by Lannefors et al. 1983, is a very strong indication of aerosol long range transport influence. The fact that similar directional dependences are found at all three sampling sites, strongly supports this suggestion.

Furthermore a comparison of the average elemental concentrations at the three sites in sector South yields a gradual northbound decrease. On the average, the Rörvik sector South concentrations are 60-70 % and Sjöängen sector South concentrations 40-60 % of the concentrations in Falsterbo. A similar comparison made between measurements in northerly air-masses shows no such behaviour - the Sjöängen values only being slightly lower.

SWEDISH AND FOREIGN CONTRIBUTIONS

In quantifying Swedish and foreign contributions to the elemental concentrations in southern Sweden, different approaches can be taken. In the OECD long range transport of air pollutants (LRTAP) study (OECD 1977) measurements of sulphur concentration levels in a vast western European network together with an emission inventory constituted the basis for meteorological models describing the western European sulphur dry and wet depositions. Furthermore this model permitted a calculation of transboundary sulphur transport in such a way that depositions in a specific (western European) country could be estimated. Thus 75% of the sulphur depositions in Sweden were calculated to originate from foreign emissions. In two publications (Shaw 1981 and Lannefors et al. 1983) using one data base, i.e. measurements in southern Sweden, the foreign component for sulphur and some heavy metals was calculated using two different meteorological models (table 2).

Having access to simultaneous measurements at three different sampling sites we use some assumptions relying only on some meteorological information and elemental concentration changes with air-mass transport path to the sampling site to calculate the Swedish and foreign contributions at the sites at Rörvik and Sjöängen. Since this technique requires no source inventory it is useful for

elements with emissions difficult to quantify. In order to limit the influences from sources like erosion and sea-spray, producing mainly coarse mode particle mass, the following discussion is restricted to the fine particle mode i.e. particles with an aerodynamic diameter $< 2 \mu\text{m}$. For the calculations the following underlying assumptions are made:

- a/ Falsterbo sector South concentrations (F_S) are considered to represent the aerosol composition that is transported in over Sweden which implies no local contamination in this sector.
- b/ Falsterbo sector North concentrations (F_N) are assumed to roughly represent the composition of the contribution from Swedish sources.
- c/ Rörvik and Sjöängen sector South samples are taken in air masses which at the time of their passage over the Swedish south coast had similar concentrations as those actually measured in Falsterbo.
- d/ The deposition velocity is equal for all components in both southerly and northerly air flows.

The geometric mean of the ratios between Rörvik sector South concentrations (R_S) and F_S and Sjöängen sector South concentrations (S_S) and F_S , respectively, give information on the combined effect of aerosol concentration losses and contributions during the transport across southern Sweden. By using the ratios between F_N and F_S a rough comparison of distance weighted impact of the sources in sector South and North at Rörvik and Sjöängen can be obtained. These calculations only include elements always found above detection limits (which excludes Cl, Ca, Cr, Cu, Br and Pb), since in the case of an element not being detected a value must be assigned which could seriously affect the geometric mean ratios. In figures 4 and 5 it can be seen that there is an element dependent difference in the ratios between R_S/F_S and S_S/F_S . From the fitted lines it is possible to extrapolate to $F_N/F_S = 0$ which means no Swedish contributions, thus indicating only foreign contributions. In this way concentration decay during northerly transport over southern Sweden can be separated from increases in elemental concentrations resulting from emissions in southern Sweden i.e. between Falsterbo and Rörvik and Falsterbo and Sjöängen, respectively. From figures 4 and 5, especially the former one, it can be discerned that the elemental composition of F_N describes the variations in R_S/F_S and S_S/F_S very well. This indicates that the assumptions made earlier are reasonable. The relative importance of the emissions in southern Sweden are found in figures 4 and 5 by subtracting the foreign contributions as indicated earlier.

Employing the described evaluation technique the foreign sector South concentrations are reduced to 40 % in Rörvik and to 30 % in Sjöängen of those in Falsterbo. Applying these foreign concentration decays to a very simple approach

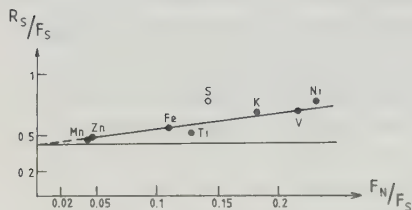


FIGURE 4. Separation of foreign and Swedish elemental contributions at the sampling site at Rörvik.

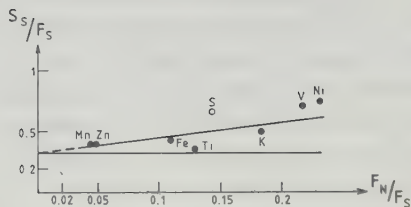


FIGURE 5. Separation of foreign and Swedish elemental contributions at the sampling site at Sjöängen.

assuming a uniformly mixed 1000 m thick boundary layer, no lateral or vertical dilution and a wind speed of 5 m/s results in a deposition velocity of 1.3 cm/s for the Falsterbo to Rörvik transport and 0.9 cm/s for the Falsterbo to Sjöängen transport. These values are higher than dry deposition velocities normally accepted for the fine mode (Garland 1978, Sehmel 1980). However as indicated by e.g. Lannefors et al. (1983) (for conditions in southern Sweden on an annual basis), wet deposition is up to an order of magnitude more efficient than dry deposition in removing fine mode oriented elements. In the light of this a deposition velocity of around 1 cm/s seems quite reasonable.

TABLE 2. Swedish fine mode ($<2 \mu\text{m}$) relative contributions (%) in sector South samples (except for Sjöängen in Lannefors et al., which are annual mean contributions regardless of transport sector.)

Element	RÖRVIK (This work)	SJÖÄNGEN (This work)	SJÖÄNGEN (Shaw 1981)	SJÖÄNGEN (Lannefors et al 1983)
S	-	-	10	20
K	35	35	-	-
Ti	15	10	-	-
V	40	55	50	70
Mn	10	15	8	-
Fe	25	25	42	-
Ni	45	55	26	50
Zn	10	15	-	-
Pb	-	-	19	30

The southern Sweden average contributions relative to the foreign contributions are listed in table 2 and are of the order of 10-50% with the lowest values for Ti, Mn and Zn and the highest for V and Ni (having the weakest

directional dependence). The percentages agree fairly well with those computed by Shaw (1981), who used a source inventory, which was later published in Monitor (1982), to calculate the magnitude of the contributions from southern Sweden.

The major part of the Swedish metallurgical industry is located north-east of the sampling site at Sjöängen (fig. 1) with one important steel mill far east and two far south of Rörvik/Sjöängen. The dominating part of the Swedish (anthropogenic) Mn and Zn emissions and also the larger part of the Fe emissions takes place in the metallurgical industries located east and north east of Sjöängen. Practically the only source of V and the dominating source (75%) of Ni is oil combustion located mainly in the most densely populated areas in southern and central Sweden. This means that a large part of the V and Ni emissions takes place in southern Sweden. A European heavy metal source inventory by Pacyna (1983) shows that the anthropogenic per capita emissions, which are used as a measure of the elemental composition, of V and Ni are much higher in Sweden than the western European average while for Mn and Zn they are lower and much lower, respectively. Unfortunately no source inventory is at hand for the elements K and Ti. Relating the location of the major source areas to the relative Swedish contributions calculated (table 2) from the approach taken in figures 4 and 5, it is quite obvious that the relative Swedish contributions are higher for elements with sources in southern Sweden.

The approach taken to separate foreign and Swedish sources does not allow calculations to be made for components such as sulphur, having both gaseous and particulate species. To be able to calculate the relative southern Sweden contribution of particulate sulphur in Rörvik and Sjöängen with this model, SO_2 concentrations have to be measured and transformation rates in southerly and northerly air flows have to be estimated. For comparison sulphur has been included in figures 4 and 5 and can be seen to deviate (being too high), especially at Rörvik, from the fitted line. The reason is probably that further transformation of long range transported sulphur dioxide takes place during its transport across southern Sweden. Applying this approach to sulphur would therefore tend to lead to the interpretation of such a transformation as a Swedish contribution, thus overestimating the Swedish contribution to the sulphur concentrations measured.

SIZE DISTRIBUTION INTERPRETATIONS - BASIC STRUCTURES

Elemental particle size distributions can be used to evaluate dominating aerosol source types e.g. erosion, combustion or bubble bursting mechanisms (see

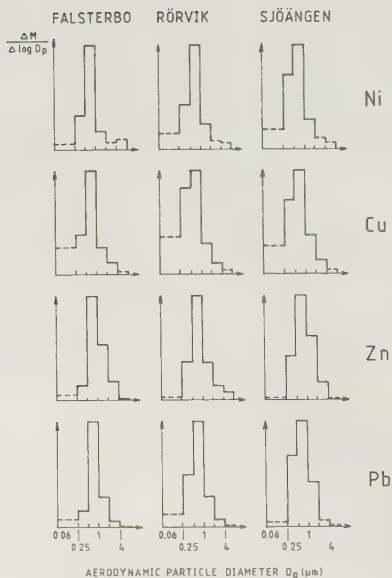
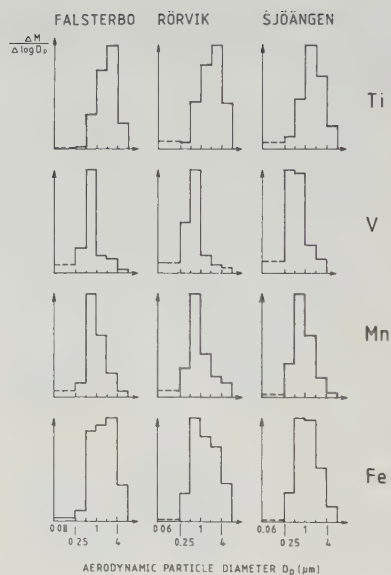
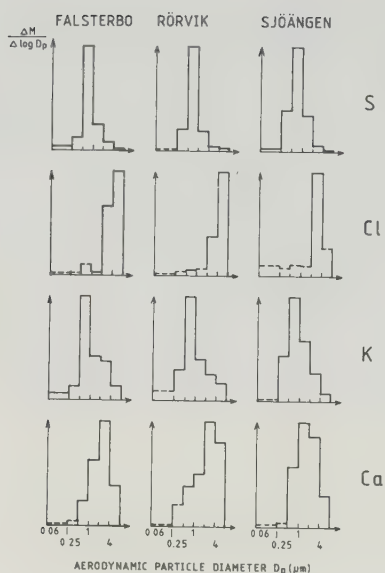


FIGURE 6a-c. Average (aerodynamic) particle size distributions (mass) for sector South during winter-time. The size distribution below 0.25 μm is unknown. A lower limit of 0.06 μm is assigned. The broken lines indicate that the values are influenced from the detection limit.

e.g. Van Grieken et al. 1976, Whitby 1978), at the sampling site. Of course factors such as sink mechanisms and atmospheric transformations also play important roles in shaping the size distribution. In fig 6 size distributions for 12 elements found in sector South during the winter period are plotted. Comparing these elemental size distributions a division can be made between fine and coarse mode (particles having an aerodynamic diameter of $2-8 \mu\text{m}$) oriented elements. The first group comprises the elements Cu, Ni, V, Pb, S, Zn, K and Mn listed in order of increasing mass median aerodynamic diameter (MMAD) and the second group, listed in the same way Ti, Ca and Cl while Fe can be placed somewhere in between. This fine - coarse mode element division is supported by the MMADs given in table 3. The elements in the fine mode group all have MMADs in the $0.5-0.9 \mu\text{m}$ range while elements in the coarse mode group have MMADs larger than about $2 \mu\text{m}$.

TABLE 3. Mass median aerodynamic diameters (μm) for sector South (winter measurements).

Site Element	FALSTERBO	RÖRVIK	SJÖÅNGEN
S	0.75	0.72	0.70
Cl	4.2	4.6	2.6
K	0.89	0.79	0.83
Ca	2.3	2.5	1.7
Ti	2.1	2.0	1.5
V	0.71	0.62	0.53
Mn	0.90	0.82	0.83
Fe	1.6	1.3	1.2
Ni	0.68	0.62	0.57
Cu	0.59	0.48	0.60
Zn	0.86	0.75	0.79
Pb	0.74	0.62	0.65

In table 3 a tendency towards decreasing MMAD from south to north in the three-station sampling network can be found for many elements. A detailed study of the size distributions in fig. 6 reveals northbound increases of the relative mass load on stage five ($0.25-0.5 \mu\text{m}$) compared with stage four ($0.5-1 \mu\text{m}$), especially for the elements V, Ni and Pb but also discernible for S, K, Mn and Zn. These changes in size distributions can be interpreted as newly formed aerosol contributions (having a lower MMAD, see e.g. Whitby 1978, Lannefors and Hansson 1980) or a preferential scavenging of larger particles during transport across southern Sweden, but can also indicate systematic cut-off differences in the different cascade impactors and effects of air humidity etc.

There are also indications of size distribution differences in the

accumulation mode between the elements. This is especially notable on the load of stage five. Compare e.g. V and Mn (fig. 6).

SIZE DISTRIBUTION INTERPRETATIONS - FINER STRUCTURES

In order to further evaluate the implications described above the multivariate statistical program package SIMCA (Wold et al. 1981) was applied to the data set. SIMCA is an interactive method and the basic concepts are that data believed to form clusters are divided into separate classes. For each class, models are created by using principal component analysis. The residuals are calculated for each object (measurement) in a class, which, quadratically added, determine a confidence interval around the model (see appendix). By comparing this interval with the distance to objects belonging to other classes (and also using other SIMCA routines) quantitative measures are obtained of:

- (1) each model's ability to describe its class
- (2) the homogeneity of the data distribution in each class
- (3) the significance of the class separation
- (4) the importance of the different variables in defining the models
- (5) the importance of the different variables in discriminating between the classes.

SIMCA applied to atmospheric aerosol data is described in more detail in Hansson et al. (in press).

Scaling, normalization and data selection

A variability scaling (mostly variance scaling is used) of the data set is in most cases appropriate prior to the application of the multivariate statistical method (see e.g. Anderberg (1973), Wold et al. (1981)). This can also be supplemented by normalizations, e.g. by using the ratios between the masses of the aerosol components to the total aerosol mass (Henry 1977). The intention here is to examine whether there are statistically significant differences in the accumulation mode size distributions ($0.25 \mu\text{m} < D_p < 2 \mu\text{m}$, corresponding to stages 3-5 in the cascade impactor) for the different elements. Therefore, prior to the variance scaling when creating class models, the data set is reorganized in two steps:

- (1) The accumulation mode size distribution for each element is calculated

using the formula:

$$s_{ijk} = x_{ijk} \left(\sum_{j=3}^5 x_{ijk} \right)^{-1}$$

x_{ijk} = measurement data
 i = sampling occasion
 j = impactor stage
 k = element

Thus the elemental size distribution for one sampling occasion is described by three points, each representing one stage in the space which is spanned by the variables. If all elements have the same size distribution the direction from the origin of all points will be the same. However, if there are differences in the size distributions for the different elements the directions to the points will differ.

- (2) To make separation only dependent on size distribution differences i.e. on the three directions as defined in step 1 above, we form:

$$c_{ijk} = s_{ijk} \left(\sum_{k=1}^M s_{ijk} \right)^{-1}$$

M = number of variables(elements)

This normalization conserves the directions from the origin to the data points determined in step 1 and the measurement space becomes orthogonal to the direction where all the coefficients are equal for the elements. This means that separations appearing after such a normalization depending only on the elemental size distribution differences. In the text c_{ijk} will be called the relative load.

In this analysis the size fractions 1-2, 0.5-1 and 0.25-0.5 μm , stages 3, 4 and 5 respectively, will be considered. A well defined group of sampling occasions is obtained if only sector South winter measurements are used (six occasions at each site). In this group there are 10 elements that are detected on all three stages mentioned above on all sampling occasions and sampling sites.

As mentioned above, there seems to be a difference in the size distributions at the Falsterbo site compared with the other two sites. This is examined by forming a training set which contains the Rörvik and Sjöängen samples, leaving the Falsterbo samples as a test set. From the former samples class models are created by the SIMCA program, one for each of the three stages considered. In table 4 it can be seen that the distances (see appendix) between the classes are large. Thus, the training set forms well separated classes, which means that there are significant differences in the size distributions between the elements at the Rörvik and Sjöängen sites. In figures 7a, 8a and 9a

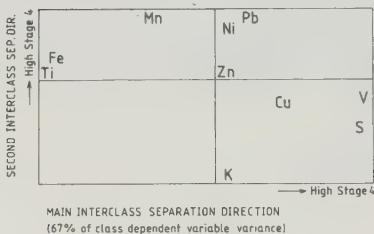
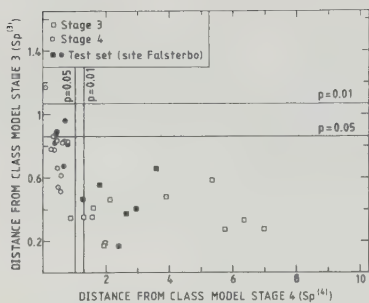


FIGURE 7. Stages 3 and 4.

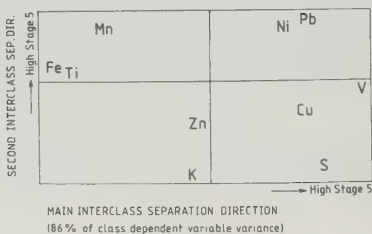
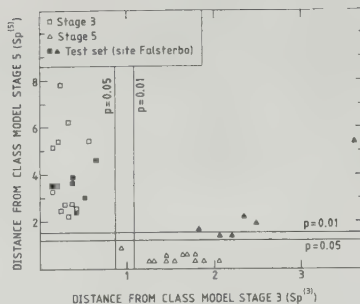


FIGURE 8. Stages 3 and 5.

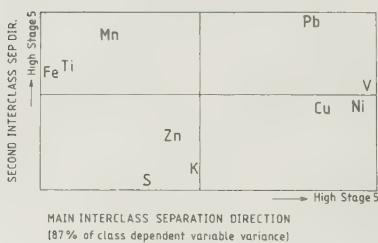
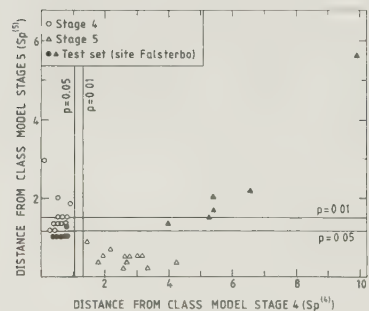


FIGURE 9. Stages 4 and 5.

FIGURES 7-9. a/ The distance from the measurements to the class models (Sp is defined in the appendix). b/ The importance of the variables (elements) in discriminating between the classes. The denotation "high stage n" refers to the direction chosen for the dependent variable. (The main and second interclass separation directions are not drawn to scale. In all cases the main separation direction accounts for the major part of the variance, while the second direction only accounts for a few percent, except for fig. 7 where the second interclass separation direction accounts for 14%.)

TABLE 4. The distances between classes compared with the distance for the 1% probability level of the classes being identical (see appendix). The sites are: F=Falsterbo, R=Rörvik and S=Sjöängen.

Site(s)	R+S	R+S	R+S	R+S	F
Stages	3,4	3,5	4,5	4,5	4,5
No of variables	10	10	10	8	8
d	5.2	5.8	3.2	3.5	7.2
$(F_{0.01})^{0.5}$	1.3	1.4	1.3	1.4	1.5

the distances for each object from the class models are plotted. Probability levels concerning measurements that have not been used to form the specific class model are indicated in the figures. These levels express the 5% and 1% probabilities of finding a measurement belonging to that class outside these distances (see appendix). Here it is evident that the discrimination between stages 3 and 4 emerges from the stage 4 model which excludes stage 3 objects. However, the discrimination acts both ways when stage 3 is compared with stage 5 and stage 4 with stage 5.

Class discriminating elements

The discrimination of the variables between two classes can be calculated with the SIMCA-routine PLS (Wold et al. 1982). In principle this is done by adding an extra variable. For the added variable all samples belonging to the first class received the same number, while the samples from the second class received a different number. In this way the added variable expresses class inclusion. The PLS-routine then calculates the combinations of the other variables that explain the variance in the added (dependent) variable, i.e. the interclass discrimination properties of the variables. In figures 7b, 8b and 9b the two first components that describe the differences in elemental composition between the stages are shown. Thus the main separators between stage 3 and 4 composition are the higher relative loads of Ti and Fe on stage 3 and, to a somewhat lower extent, the higher relative loads of V and S on stage 4 (fig. 7b). Judging from the size distribution (figure 6) the separation is mainly caused by erosion products having an important influence on Ti and Fe stage 3 concentrations. This picture does not change much when stage 3 is compared with stage 5, although it can be seen that the separation ability is somewhat increased for Ni, Pb and V (fig. 8b). In figure 9b it can be seen that when stage 4 is compared with stage 5 the discrimination due to the erosion influenced elements Ti and Fe is considerably decreased. Instead we find a polarization where the relative loads on stage 5 are high for V, Ni, Cu and Pb.

However, Ti and Fe still work as separators which can be due to fine particulate erosion products on stage 4. Therefore Ti and Fe are excluded and the measurement space recalculated according to the schedule above, forming new class models for stages 4 and 5 for the remaining 8 elements. The distance between the new stage 4 and 5 classes is 3.5 (table 4), and as shown in fig. 10 these elements are clearly polarized in the main interclass separation direction.

Test set application

Before evaluating the soil influence on the accumulation mode, the Falsterbo measurements will be applied as a test set to the training set models to find out whether there are any significant differences. Figures 7a, 8a and 9a show that the Falsterbo stage 3 and 4 composition, in contrast to stage 5, fit the respective class models very well. It can also be seen that Falsterbo stage 5 does not fit any other of the models. Comparing the stage 5 relative composition at site Falsterbo with those from the Rörvik and Sjöängen sites it is found that the relative loads of V, Ni and Cu are even higher on stage 5 at the Falsterbo site. This implies, together with the fact that the loads on Falsterbo stage 5 are generally lower for all elements (fig. 6), that the impactor used at the Falsterbo site has its stage 4 to 5 cut-off at a somewhat finer particle diameter. This is further supported by the fact that the Falsterbo stage 4 measurements are somewhat closer to the stage 5 model than the measurements at the two other sites (fig 9a). In these regions of the size distribution dm/dD_p is large and calculations show, under conditions of constant flow rate, that if the stage 4 jet diameter is 5% too small the cut-off diameter will decrease by 8%. (The stage 4 jet diameter is not flow-rate limiting.) Under such circumstances minor differences between different samplers, such as the differences in MMAD in table 3, easily arise. Therefore these differences will not be considered further. However, even if there is not exactly the same cut-off between stages 4 and 5 at the Falsterbo site, this is not an obstacle for the comparison of relative loads.

Class models are formed for the Falsterbo site in the same way as previously for the sites at Rörvik and Sjöängen, but with the restriction that only stages 4 and 5 are compared. The group of stage 5 objects contains one outlier, which will be treated separately. Class models are then formed for the remaining samples. The distance between the classes is 7.2 which, also taking the low number of objects into account, is a very large class separation (table 4). In figure 11a the elemental interclass separation properties can be seen.

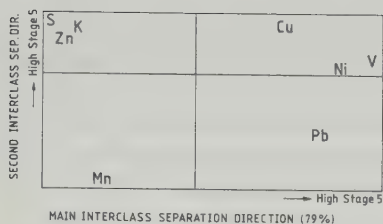


FIGURE 10. The importance of the variables in discriminating between the classes for stages 4 and 5 at the sites at Rörvik and Sjöängen (Ti and Fe excluded). See also figures 7-9 b.

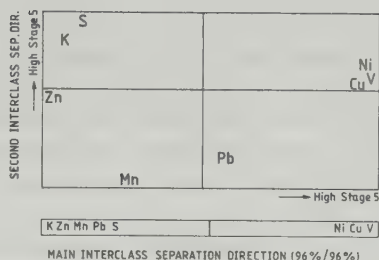


FIGURE 11. The importance of the variables in discriminating between the classes (see also figures 7-9 b) at the Falsterbo site between:
a/ stages 4 and 5.
b/ stage 4 and the stage 5 outlier.
(for the latter only one direction.)

For the Falsterbo stage 5 outlier, elemental separation from class model stage 4 is found in figure 11b. The main difference between the class model stage 5 and the outlier is the lower relative load of Pb for the latter.

There is a significant difference in the elemental relative load between stage 4 and stage 5 at all three sampling sites. Hence there must be processes creating elemental size distribution differences in the accumulation mode. By comparing figures 10 and 11 it can be seen that there is also a striking similarity between the separation patterns at all three sites. The relative loads of V, Ni and Cu are high on stage 5 while they are low for S, K, Mn and Zn. For Pb there is no definite trend, although it is closer to the former group of elements.

Influence of natural sources

In order to further evaluate the reasons for the size distribution differences observed, some simple calculations were undertaken. By calculating the geometrical mean of the ratio (stage 5/stage 4) for an element (using the raw data) in the low MMAD group divided by the same ratio for an element belonging to the other group, the typical value obtained is greater than 2 having a geometric standard deviation of less than 2. This means that, if

natural sources like sea-spray or erosion products causes these size distribution differences, they must contribute approximately 50% or more for one particular element on stage 4 while stage 5 is not influenced. In order to check this hypothesis some simple calculations can be made. Ti has a size distribution that suggests a large soil influence (fig. 6). Making the assumptions that all Ti measured on stage 4 is soil derived, while stage 5 is not influenced, will certainly result in a large overestimation of the soil influence on the (stage 5/stage 4) relation. Using Ti as a tracer and the soil composition of Bowen (1966) to calculate the soil derived stage 4 amounts under the above mentioned conditions results in the following proportions from soil: 30% for Fe, 10% for K, 5% for Mn and still lower for the remaining elements. Therefore it can be concluded that the soil influence can be neglected in the separation pattern demonstrated in figures 10 and 11.

In order to make similar calculations of the sea-spray influence Cl can be used as a tracer. However, the accumulation mode Cl concentrations may, as mentioned in table 1, be affected by the pH-value of the aerosol. Therefore we chose to use the coarse mode concentrations (mass) and estimate the accumulation mode concentrations with the assumption that the accumulation mode sea-spray mass is equal to the coarse mode mass, which according to earlier measurements is an overestimation of the influence on the accumulation mode (see e.g. Mészáros and Vissy (1974), Jaenicke and Schütz (1978)). From the estimation of the accumulation mode Cl concentration, the sea-spray contributions of other elements are calculated using the sea-water composition given by Pytkowics and Kester (1971). The calculations result in about 2% of the K and 0.5% of the S measured originating from sea-spray. Despite the simplicity of the calculations (e.g. enrichment is not considered) it can be concluded that sea-spray can not be responsible for the separation found.

Another natural source mentioned in the literature which can possibly make a contribution is vegetation. Went et al. (1967) reported a correlation between the Aitken condensation nuclei counts and the density of the underlying vegetation. Crozat (1979) suggests that particles are created during guttation (which is a process appearing under extremely humid conditions, when water cannot evaporate as rapidly from the leaves as it is taken in by the roots. As a result, root pressure may become great enough to force water out of the leaves.), but other processes are also suggested (Schnell and Vali 1973, Beauford et al. 1976). The particles released during guttation have a high K content (Crozat 1979). However, there is not much known about the magnitude of the aerosol production from vegetation. Neither can it be concluded whether the main part of the vegetation emissions results in particles with a size distribution like those from soil and sea-spray or if they participate in

creating the accumulation mode particles.

Anthropogenic sources, transport and transformation mechanisms

The ubiquitous fractions of soil and sea-spray can not be responsible for the element dependent differences in size distributions in the accumulation mode. We therefore suggest, with reservations for the influence of other natural sources, that the size distribution differences observed originate from anthropogenic sources. According to calculations by Whitby (1978) freshly formed aerosol particles coagulate with accumulation mode particles in a short period of time, relative to coagulation between accumulation mode particles. The fresh aerosol preferentially coagulates with the finer accumulation mode particles, i.e. where the largest particle surface area is found. This process should, in the general case, not give rise to systematic elemental composition differences between particles of different sizes, unless there is a systematic change in the elemental composition of the emissions along the air mass transport route. When comparing the anthropogenic emissions in Sweden with those in continental Europe and Great Britain (see earlier section) it is found that the emissions of V and Ni in Sweden are relatively large compared with the other elements discussed. This could be the reason for the relatively larger amounts of these elements on the finer accumulation mode particles at the two northerly sampling sites. However, the similarity in separation pattern at all three sites (figures 10 and 11) contradicts this explanation. Hence, the size distribution differences observed can not be related to differences in transport distances.

Difficulty in understanding the results obtained arises from the fact that all elements measured, except sulphur, are micro-components in the aerosol matrix. This means that they probably do not affect the chemical properties of the aerosol, more than to a limited degree, unless they serve as catalysts for important chemical reactions in the atmosphere. However, these elements can be used as tracers of emission sources, and thereby be indicators of the presence of macro-components in the aerosol matrix. V and Ni are to a large extent, together with large amounts of S, emitted from oil combustion sources. Despite this fact we find V and Ni in the group with low relative sulphur content. This means that the aerosol, to a large extent, has received its S content after the emissions, i.e. the S in these measurements is mainly a secondary aerosol component. Therefore there must be reactions available for the SO_2 transformation to the particulate phase. One important SO_2 transformation path is oxidation in the droplet phase (Beilke and Gravenhorst 1978, Möller 1980), especially in wintertime at high latitudes (Shaw and Rodhe 1982). For this

transformation the hygroscopic properties of the particles are very important. Particles with a large proportion of insoluble species in the matrix will grow less with increased humidity (Winkler 1973). With a strong influence from emission sources delivering large amounts of water-insoluble particle-bound species the SO_2 transformation path above will be less efficient, thus resulting in a lower aerosol S content.

This suggestion can explain both the systematic differences in size distribution between the elements and the higher relative content on the larger accumulation mode particles of the macro-component, and to a large extent secondary aerosol sulphur.

CONCLUSIONS

The study demonstrates a strong influence of long range aerosol transport from continental Europe on heavy metal and sulphur concentrations in southern Sweden. These large scale events are demonstrated by a strong directional dependence of the elemental concentrations, i.e. considerably higher heavy metal and sulphur concentrations in air masses originating over the European continent and Great Britain than in north Atlantic air masses.

Employing a new technique, which requires no emission inventories, to separate the contributions within the measurement network from outside contributions resulted in that the contribution from southern Sweden in the fine mode ($D_p < 2 \mu\text{m}$) being of the order of 30 - 50% for K, V and Ni while still lower for Ti, Mn, Fe and Zn. The results are in good agreement with earlier calculations of the foreign contribution to southern Sweden.

Size distribution evaluations indicated that the elements Cu, Ni, V, Pb, S, Zn, K and Mn, listed in order of increasing mass median aerodynamic diameter, mainly originate from high temperature sources (e.g. combustion), while the size distributions of elements such as Cl, Ca and Ti indicate dominating mechanical source processes (e.g. sea-spray generation and soil suspension). Both source types seem to be important contributors for Fe.

Multivariate statistical evaluation showed, with high significance, that there are systematic differences in the elemental composition between different particle size fractions in the accumulation mode in air masses that have passed over the large source areas in Europe when arriving in over southern Sweden. The separation pattern between these fractions is almost identical at all three sampling sites, and can not be interpreted as the influence of erosion products or sea-spray. S, V and Ni are normally assumed to originate from the same sources (fossil fuel combustion). Despite this, the latter two elements were

found on the smaller accumulation mode particles to a larger extent (relatively) than S. A suggested explanation for the observed covariation between S, K, Mn and Zn is the transformation of SO_2 on hygroscopic particles (containing these elements to a larger extent) being a more efficient process than SO_2 transformation on less hygroscopic V- and Ni-containing particles and thus resulting in size distribution differences although the latter elements are emitted simultaneously with S.

A multivariate statistical evaluation technique using the program package SIMCA has been shown to be a very capable and easily used aid in the evaluation work. Direct quantitative statistical measures were obtained of the significance that different classes (e.g. size fractions) are separated, and also which elements work as separators. Altogether SIMCA has proven to be a very useful tool in the evaluation work.

ACKNOWLEDGEMENTS

We are very grateful for sampling assistance at the three sampling sites. Valuable comments on the manuscript were provided by K.R. Akselsson, J. Heintzenberg, H. Rodhe and S. Wold who's assistance is gratefully acknowledged. This work was partly supported by the National (Swedish) Environment Protection Board.

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In this appendix the basic formulae of SIMCA are given. We also refer the reader to Wold et al. (1981).

For objects (measurements) believed to form clusters, models (class models) are created by principal component analysis, i.e.:

$$x_{ik} = \alpha_i + \sum_{a=1}^A \beta_{ia} \theta_{ak} + \epsilon_{ik}$$

i = index of the variable (element)
 k = index of the object (occasion)
 x = data
 α = coordinate for class centre in element space
 β = principal component
 θ = coefficient
 ϵ = residual
 A_q = dimension of class model q
 a = index of the principal component

The dimensions of the class models are determined by cross-validation (Wold 1978).

The residual standard deviation for the objects applied to their own class model (q) is expressed:

$$S_0 = \left(\sum_{i=1}^M \sum_{k=1}^{N_q} \epsilon_{ik}^2 \right)^{0.5} \left((m-A_q)(N_q-A_q-1) \right)^{-1} \quad \begin{array}{l} M = \text{number of variables} \\ N_q = \text{number of objects} \\ \quad \text{in class } q \\ m = \text{dimension of} \\ \quad \text{measurement space} \\ \quad \text{(in our case } m=M-1) \end{array}$$

The distance from a point (p) to a class model in which the point has not been used to shape the model is given by:

$$S_p^{(q)} = \left(\sum_{i=1}^M \epsilon_{ip}^2 (m-A_q)^{-1} \right)^{0.5}$$

An F-test is performed to calculate confidence intervals for a certain class q . For

$$F(m-A_q, 0.5(m-A_q)(N_q-A_q-1))$$

the distance corresponding to a certain probability level of finding an object belonging to the class in question (that has not been used to shape the

specific class model) at a greater distance, is given by:

$$S_p^{(q)^2} = F_q (S_0^{(q)^2})^{-1}$$

(From this test the probability levels in figures 7a, 8a and 9a were calculated.)

The distance between two classes (see table 4) r and q is expressed:

$$d_{r,q} = ((S_q^{(r)^2} + S_r^{(q)^2}) (S_0^{(r)^2} + S_0^{(q)^2})^{-1})^{0.5}$$

$$\text{where } S_q^{(r)} = \left(\sum_{i=1}^M \sum_{p=1}^{N_r} \epsilon_{ip}^{(q)^2} ((M-A_r)N_q)^{-1} \right)^{0.5}$$

is the residual standard deviation for the objects of class q when applied to the model of class r .

$d_{r,q}^2$ is approximately F-distributed (Wold and Sjöström 1977):

$$F(0.5((N_r - A_q)(m - A_q) + (N_q - A_r)(m - A_r)), 0.5((N_r - A_r - 1)(m - A_r) + (N_q - A_q - 1)(m - A_q)))$$

From this F-test a measure is obtained of the probability of achieving a certain distance if identical classes are compared (see table 4).

A NON-SELECTIVE PRECONCENTRATION TECHNIQUE FOR WATER ANALYSIS BY PIXE

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ABSTRACT

A non-selective preconcentration technique for water (such as rain water) with especially low concentrations of dissolved constituents is proposed. By means of a nebulizer the water is sprayed to a droplet aerosol, which is dried with clean dry air. The dry aerosol particles (diameter about 1 μm) are deposited on a thin polystyrene foil in a multijet impactor. The set-up is thoroughly described. The best detection limits achieved for the present set-up are approximately 0.1 ppb (ppb = $\mu\text{g/l}$) for a 10 ml sample. A recovery test is shown and discussed. Comparisons with other non-selective preconcentration methods for X-ray analysis are also made.

BACKGROUND

Interest in the chemical composition of different natural waters has increased very much during the last decade due to greater awareness of the problem of pollution. For example, when studying the atmospheric aerosol rain naturally becomes interesting, as the main part of the atmospheric aerosol, natural as well as anthropogenic, is deposited through rain.

The properties of Particle Induced X-ray Emission (PIXE) analysis as a fast multi-elemental analytical method with high sensitivity have proved to be very useful for studies of the atmospheric aerosol (1,2). In order to follow the same broad range of elements in the bio-geo-chemical circulation it would be advantageous to use the same analytical method, apart from the other advantages given by PIXE shown in several different applications.

However, in most kinds of water the concentrations are quite low for several elements, around and below the ppb-level. Thus multi-elemental preconcentration techniques are needed. A comprehensive review of various preconcentration methods for analysis by X-ray spectrometric techniques has been made by Van Grieken (3). Here only comparable elemental non-selective preconcentration methods suitable for analysis by PIXE will be discussed, i.e. all elements present in the sample are concentrated with the same efficiency onto a thin clean backing. Element-selective techniques developed especially for PIXE are described elsewhere (3,4).

The most common non-selective preconcentration methods for X-ray spectrometric analysis are

- a) dropping and drying a small amount of water on a thin foil
- b) "vapour filtration" of the water vapour through a thin membrane, i.e. the Purdue method (5).

A new preconcentration method for obtaining a dry sample on a thin backing will be presented. The water is first sprayed into a dry air stream; the water droplets are there dried into a fine aerosol consisting of dry particles. The air is then pumped through an impactor and the aerosol particles are deposited on a thin polystyrene foil, supported by a glass plate. This technique will be described in detail below.

When comparing the preconcentration techniques presented above with each other

or with similar preconcentration techniques for PIXE analyses of a specific type of water, the following points should be considered.

- a) the relative concentration of non-volatile elements
- b) backing properties such as thickness, impurities, acid resistance, mechanical strength and beam resistance
- c) sample homogeneity, crystallization
- d) amount of water used for the preparation
- e) losses during the preparation and achieved effective sample area (beam area)
- f) contamination problems

These points will together give a basis, independent of a specific PIXE-analysis set-up, for choosing the best method for the water that is to be analysed. In the PIXE-analysis the properties of the specific PIXE set-up will then, of course, affect the resulting absolute detection limits.

EXPERIMENTAL

Experimental arrangement

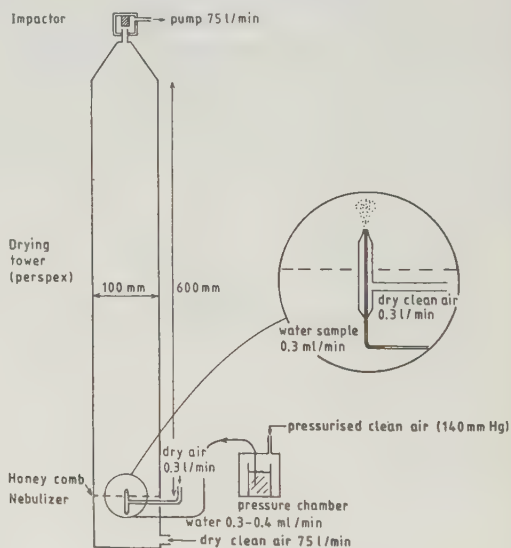
Spray-drying techniques have been used in many different applications, even in industrial processes, e.g. for producing dry milk powder. The technique for preparing uniform thin film deposits ($10\text{--}1000\text{ }\mu\text{g}/\text{cm}^2$) for X-ray analysis was first described by Jolly and White (6). Kellog et al., (7) have used a variation that is similar to the technique proposed by us. The authors mentioned above report water analysis at the ppm-level. We have tried to optimize the spray technique to obtain the best possible detection limits for water with a low amount of matrix mass, such as rain water, by taking into consideration the points given above.

In our set-up a concentric nebulizer, type Meinhard (Kontron AB), (see fig 1), designed to be used in Inductively Coupled Plasma (ICP) analysis, has been used. Characteristic of this type of nebulizer is low gas and liquid flow, about $0.3\text{--}1\text{ l/min}$ and $0.1\text{--}1\text{ ml/min}$, respectively. It is made of borosilicate glass. As shown in figure 1 the nebulizer is placed in an aerosol drying tower. A clean dry ($\text{RH} < 1\%$) air stream is blown through the tower to dry the droplet aerosol to a fine dry aerosol, which is collected in an impactor at the top of the tower. The droplet aerosol has a mass median aerodynamic diameter (MMAD) of about $50\text{ }\mu\text{m}$.

The non-volatile mass concentration of rain water is about 10 ppm. The dry aerosol obtained for rain water will then have an MMAD of about $1\text{ }\mu\text{m}$.

To collect the aerosol a multijet impactor was constructed and used. The impaction surface is a thin polystyrene film ($30\text{ }\mu\text{g}/\text{cm}^2$) on a glass plate. Before irradiation the film is removed from the glass plate and mounted on an aluminum frame using a special procedure (8). To reduce the bounce-off problems the film has a thin layer of paraffin. The impactor has 8 holes distributing the aerosol over an area of about 0.5 cm^2 , suitable for an 8 mm beam in a PIXE set-up. It is possible for most PIXE set-ups to reach this beam size.

Figure 1. Experimental set-up for preconcentration of water through spray drying.



To make the water feeding system as short and as simple as possible in order to avoid contamination a special pressure system was constructed. The plastic bottle, in which the rain water was collected, was placed in a pressure chamber with an over-pressure of 140 mm Hg. The water is forced through a narrow polyethylene tube directly into the spray nozzle. The tube and the spray nozzle can easily be cleaned by forcing acid through the system instead of water.

Aerosol characterization

To check the efficiency of the aerosol generation and the transport at different liquid and air flow-rates, various aerosol characterization instruments were

used. An Aerodynamic Particle Sizer (APS, TSI 3300) was used to measure the dry aerosols' aerodynamic size distribution in 50 size fractions between 0.5 and 15 μm aerodynamic diameter. An Electrical Aerosol Analyzer (EAA, TSI 3030) was used for size classification of the submicron part of the aerosol.

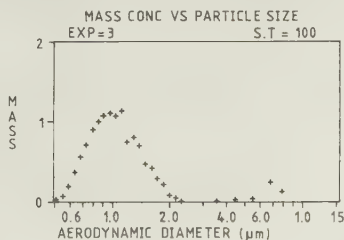
Recovery and contamination test

To evaluate the sensitivity, detection limits and possible contamination problems, especially when working with rain water, a "synthetic" rain water was prepared. The concentrations of the macro-constituents were chosen to be the same as the Swedish yearly mean values (pH=4) (9,10). Several metals were also added at concentrations of 5 ppb. Several 10 ml aliquots of this spiked synthetic rain water were preconcentrated with the experimental set-up described above and the polystyrene films were analysed with PIXE. To check "memory" effects in the system clean water was run before, between and after the rain water samples. The macro-elements present were S, Cl, K, Ca and Fe in concentrations ranging from 1000 to 100 ppb. The micro-elements, all present at a concentration of 5 ppb, were Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn and Pb.

RESULTS

Due to the high air turbulence introduced by the nebulizer in the drying tower, deposition of the aerosol on the tower walls cannot be avoided. The best mass transmission of the aerosol obtained was about 30 % at the flow-rates given in figure 1. The particle size distribution for the dry aerosol for these flow-rates was found to have its maximum at about 1 μm (see fig. 2). Variations in the total concentration of dissolved constituents in the sample gave varying aerosol size distributions and thereby varied the properties of the dry aerosol, e.g. varying transmission and impaction efficiency. Thus an internal standard has to be used.

Figure 2. Particle size distribution for the mass concentration of the dry aerosol.



The detection limits found for a 10 ml sample run with our experimental set-up are presented in table 1 together with yearly mean values for rain water in Sweden. For this sample the recovery was 18 %. Even at this rather low efficiency only three elements, Ga, Ag and Sb, have yearly mean values below the attainable detection limits. The elements Mo, Cd and Ba have detection limits comparable with their yearly mean values.

Table 1. Achieved detection limits (DL) and comparison with yearly mean values (YM) found for rain water in Sweden (10).

Parameters: 10 ml sample. Backing: polystyrene. Charge: 100 μ C.

Current: 200 nA, Absorber: 340 μ m. Mylar with hole. (ppb = μ g/l).

Element	DL(ppb)	YM(ppb)	YM/DL
S	3	1100	370
Cl	2	640	320
K	0.8	120	150
Ca	0.7	250	360
Ti	0.1	6	60
V	0.08	3	38
Cr	0.06	1	17
Mn	0.07	10	143
Fe	0.08	100	1270
Co	0.2	-	-
Ni	0.07	2	29
Cu	0.08	5	63
Zn	0.09	25	278
Ga	0.3	0.1	0.3
As	0.4	1	2.5
Se	0.08	0.3	3.8
Br	0.1	10	100
Rb	0.2	0.6	3
Sr	0.1	0.8	8
Y	0.5	-	-
Zr	0.2	0.5	2.5
Nb	0.2	-	-
Mo	0.3	0.3	1
Ag	0.4	0.2	0.5
Cd	0.3	0.3	1
Sn	0.5	2	4
Sb	1.6	0.05	0.03
Ba	5	5	1
W	3	-	-
Pb	0.5	20	40

The test with the synthetic rain water showed a recovery varying between 6 and 18 %. The increased losses, compared with those found with our aerosol measurement system, are probably due to particle bounce-off in the impactor. By looking at the relative elemental concentrations we could follow losses and contamination. Losses were found for only one element, chlorine, due to the acid aerosol. As found by Heintzenberg et al., (11) decreasing the pH of the aerosol gives an increased loss of chlorine due to gaseous hydrochloric acid being formed. Contamination was found for the elements Cu, Zn, Sn and Pb. The impaction nozzle which is made of brass is a suspected contamination source. The other elements showed a reproducibility of between 7 and 15 % for 10 samples, run in 3 series.

DISCUSSION

The present set-up is a result of several different approaches to generating a droplet aerosol, drying it and depositing it on an appropriate backing.

The set-up can be discussed and compared with other methods by using the points given in the section entitled background.

- a) Rain water has a rather unusual composition because of its very low non-volatile mass (10 ppm) and many elements are present far above 1 ppm in the dry matrix (see table 1). Thus X-ray analysis will be very suitable and reveal the presence of most elements without any further preconcentration.
- b) The backing chosen is, compared with most other backings, very thin, clean and acid resistant and can withstand a beam current of 200 nA with an 8 mm beam. This influences the detection limits directly and makes the polystyrene foil favourable compared with the membranes used in "vapour filtration", i.e. the Purdue method. Two membranes often used are Cellophane and Cuprophane, which are 25 and 8-10 μm thick respectively. Both are only resistant to relatively dilute organic acids (12). However, if the water is not acidified considerable losses of the trace elements (low ppb range) can be expected (13). Thus acid resistance is a very important property of the backing.
- c) Crystallization problems are severe when samples are dropped onto a thin foil. The formation of crystals can cause difficulties due to X-ray absorption. The maximum amount it is possible to drop onto a film is about 100 μl . By spraying the water and drying the droplet aerosol a fine powder is obtained. In our set-up we obtained an MMAD of 1 μm , However, the aerosol is

unevenly distributed on the impactation surface. A necessary improvement in the set-up is a moving impactation surface. Thus a more homogeneous deposit will be achieved. The bounce-off will also be decreased and thus the efficiency will increase. The Purdue method produces a good homogeneous sample.

- d) The amount of water used is rather small for all methods discussed. With dropping techniques only about 100 μ l could be used. Preconcentration by evaporation before the sample is dropped could, of course, be used. Tanaka et al., (14) report detection limits of about 1 ppb for dropping 20 μ l rain water on Mylar for PIXE analysis. The tests with 10 ml in this study give very good detection limits. The preparation time was 30 minutes. For this type of water the Purdue method requires roughly 30 times more sample mass deposited on the membrane, due to its thickness, to achieve approximately the same detection limits. These calculations concern the thicker Cellophane. As the efficiency was 18 % in our experiment, this gives an amount of about 54 ml of water for the Purdue method. It will then take about 6 days to prepare a sample. In this very rough comparison impurities in the backings are not considered. The comparison should be performed experimentally with the same type of water.
- e) For both the dropping and the Purdue method a 100 % recovery is reported (5,14). The sample area is easily kept inside the beam area in both cases. The spraying technique still suffers from unnecessary losses. However, the efficiency will probably not exceed 30 - 40 %. The sample deposit obtained in the present set-up is rather inhomogeneous. However, by slowly moving the impactation surface it is possible to obtain a more even deposit (15). Thus the beam area could be used much more efficiently. This will also mean that the bounce-off will decrease. It is estimated that the detection limits would be reduced by a factor 2.
- f) No contamination problems are reported for dropping and the Purdue method. We still have problems with contamination for some elements. The impactation nozzle is the most probable source of contamination as it is made of brass. Further investigations will be made with other materials. Further efforts to follow proper clean procedures will, of course, be made.

CONCLUSIONS

X-ray analysis has proved to be a very feasible method for non-selective analysis of water with low matrix content such as rain water.

The method proposed in this experiment shows very good detection limits compared

with expected concentrations in rain water. The possibility of decreasing the detection limits by a factor 2 seems good.

Compared with dropping and vapour filtration (the Purdue method) the proposed method seems favourable for water with low mass concentration. For water with higher mass concentration the Purdue method may be more favourable.

ACKNOWLEDGEMENTS

Valuable comments on the manuscript were provided by K.R. Akselsson, K. Malmqvist and S.A.E. Johansson. Excellent typing was provided by R.-M. Akselsson. This work was partly supported by the National (Swedish) Environment Protection Board.

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A MICROCOMPUTER-CONTROLLED TWO-FRACTIONATING AEROSOL SAMPLER FOR OUTDOOR ENVIRONMENTS.

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ABSTRACT

A microcomputer-controlled aerosol sampler has been constructed to give an optimized sampling and analysis system together with Particle Induced X-ray Emission (PIXE) analysis for measurements in outdoor environments.

The principles on which the presented sampler is constructed, aerodynamically, mechanically and electronically are thoroughly discussed.

The presented prototype has a capacity of 70 samples at the maximum flow rate (5 l/min). The aerosol is collected in two size fractions. The larger particles are collected on an impactor stage and the smaller particles are caught on a filter after the impaction stage. Due to the mechanical construction and the well known characteristics of the impactor it is easy to vary the cut-off diameter and the deposition area on the filter to suit the demands of the specific sampling situation. This flexibility can also be used to obtain the best possible detection limits.

The results of tests carried out on the present prototype to investigate internal losses, impactor characteristics and filter efficiency are presented. At the maximum flow rate the total losses, including wall losses, bounce-off and filter leakage even at high mass loadings, are in the 5-15% range for particle sizes between 0.05 and 10 μm .

INTRODUCTION

During the last decade extensive development of more sophisticated aerosol samplers for outdoor environments has taken place. The early types of simple total aerosol samplers (e.g. the high volume samplers) were found not to be very well suited to new analytical methods. The requirements for certain standards for sampling aerosols grew with increasing knowledge of physical and chemical properties of, for example, the atmospheric aerosol.

Different X-ray spectrometric analytical methods such as X-ray Fluorescence (XRF) and Particle Induced X-ray Emission (PIXE) proved to be very useful tools in the field of research on the atmospheric aerosol (1, 2). PIXE has in particular been used in studies of the elemental composition of the atmospheric aerosol with high time and size resolution, which has given basic knowledge about the transport, transformation and deposition properties of heavy-metal-containing aerosols (3, 4, 5).

Several aerosol samplers broadly suitable for the analytical technique have been used in studies concerning the atmospheric aerosol. The dichotomous sampler (6) for XRF and the continuous filter sampler (the streaker) (7) and the Battelle cascade impactor for PIXE are some of the most frequently and successfully used samplers.

Investigations concerning the physical properties of the atmospheric aerosol gave strong evidence for a trimodal lognormal particle size distribution. The components of the mass distribution containing most of the mass are the accumulation and coarse modes (8). The two modes often have different source origins. The latter is mostly connected with mechanical processes such as sea-spray generation and soil suspension while the former contains large portions of particles from high temperature processes, e.g. combustion. Hence, the chemical compositions of these modes differ. Together this makes separate collection necessary. The cut-off between the coarse and the fine mode is usually found to be in the region of 1.5 to 2.5 μm (8,9).

Exposure of humans and deposition, on for example vegetation, are other important processes to be considered in the sampling of aerosols. The deposition rate on different kinds of vegetation is not well known, since other parameters besides particle size distributions influence the deposition processes, such as surface characteristics and meteorological factors.

The deposition processes in the human lung have been measured and calculated in many different studies (10, 11). As a result of these and other similar reports a convention has been proposed by the Ad hoc Working Group appointed to ISO technical committee 146 (12) for application in the sampling of airborne particles. The convention is thoroughly discussed by, for example Ogden (13) and Lippmann et al (14). The 50 percent cut-off of the ambient particles (not inspired) for the alveolar convention of the British Medical Research Council (BMRC) is $4.5\text{ }\mu\text{m}$ and for the American Conference of Governmental Industrial Hygienists (ACGIH) is $3.2\text{ }\mu\text{m}$, for the thoracic convention we have $8.7\text{ }\mu\text{m}$ according to both the BMRC and the ACGIH ($10\text{ }\mu\text{m}$ when 50% cut-off of the inspired fraction). For groups other than healthy adults the 50% cut-off diameter is $2.2\text{ }\mu\text{m}$ for the alveolar convention (see fig. 7).

By compiling this knowledge about the requirements for concentration data in specific particle size fractions it can be concluded that two fractions are needed. One fine particle fraction with no lower cut-off, and a cut-off towards the coarse fraction. The cut-off between the fractions can be chosen to be between 2 and $5\text{ }\mu\text{m}$ depending on the specific purpose of the sampling. The upper cut-off for the coarse mode is for hygienic reasons proposed to be $8.7\text{ }\mu\text{m}$. The study of the total coarse mode or particles under consideration in the extra thoracic convention ($5\text{ to }150\text{ }\mu\text{m}$) (12) is very complicated due to the great difficulties in sampling particles with aerodynamic diameters larger than $15\text{--}20\text{ }\mu\text{m}$ in an unknown wind field.

The concentrations in aerosols can vary several decades in different atmospheric environments, e.g. when going from arctic to urban air. It is thereby very convenient if the sample mass per unit area can be controlled, in order to obtain lowest possible detection limits in the analysis, by changing the flow rate and/or changing the deposition area.

Other properties of importance in constructing an "allround" sampler are facilities for automatic sequential sampling, and control and/or recording of the flow rate during sampling. The degree of automation should be high enough for the sampling strategy to be as free as possible from constraints caused by the sampler. Of course high reliability is also of great importance.

TECHNICAL DESCRIPTION

Principles

As a consequence of the considerations discussed above a sampler was constructed to collect two size fractions. The upper cut-off for the coarse fraction is determined by the inlet, and will not be discussed in this paper. The sampler should allow sampling of 10 μm particles without significant internal losses.

To define the cut-off between the coarse and fine fractions an impactor was chosen on the grounds of its well known characteristics (15). When a change in cut-off is required it is relatively easy to modify the impactor without causing any significant change in the particle losses. The conventional impactor is often rejected due to the problem of particle bounce-off. This problem cannot be completely solved by using an adhesive grease, because the particle to particle bounce will increase during the sampling. If the aerosol is dry bounce-off can cause very large errors (16). A very good solution to this problem has been proposed and experimentally verified by Reischl and John (16). They used a silicon oil with low viscosity which was continuously fed to a porous impaction plate during sampling. The oil did not only wet the impaction plate but also the particle, due to its low viscosity. With this system the bounce-off was reduced to below 1%. In a basic study Dahneke (17) has shown that the particle bounce-off is directly related to the particle velocity and can be reduced by decreasing the impaction jet velocity.

For the fine particle collection a filtration stage was chosen. To facilitate repositioning for a new sample and later analysis it is favourable to use a strong thin membrane filter. Nuclepore has been found to suit both the analysis as well as the sampling procedure (7). In the "streaker" sampler the Nuclepore filter is used together with a very simple mechanical device, which makes it possible to collect many samples on one filter (7).

A major drawback with the Nuclepore filter is significant pore clogging caused by aerosols with high particle concentrations within certain size fractions, especially very fine particles (18). The flow rate has to be checked and if possible controlled during sampling. The strategy used for the present sampler is to compare the flow rate with a preset value. If necessary the sampling is stopped and continued on the next fresh sampling area on the filter. The time at which the sample was changed is recorded.

The maintenance of the sampler, manual changing of filters, manual checking of flow rate, pumps and so forth, are today often the most expensive and limiting part of the sampling programs. Therefore we have made the filters large enough to accommodate many sample positions. To utilize the filters as efficiently as possible the sample area for each sample, as well as the distance between different samples can be changed for different flow rates.

Mechanics

The aerosol enters through the impactor nozzle which is an 8-hole multijet nozzle for the maximum flow rate of 5 l/min. The jet holes are 1.1 mm in diameter. At a flow rate of 5 l/min the nozzle will give a cut-off at about $2\text{ }\mu\text{m}$ aerodynamic diameter. The multijet is preferred due to the lower air jet velocity (see above) and the larger area of deposition. A Nuclepore filter is chosen for the deposition foil. The filter strip is glued on to a plastic frame ($2.5 \times 20\text{ cm}^2$). Four frames with impaction foils together form a ring and are supported on the side of a cylinder. Parts of this surface are made of porous plastic, which can be soaked in low viscosity silicon oil. The oil is then drawn out to the deposited aerosol through the filter by capillary forces. Inside the cylindrical impaction surface there is a second concentric cylinder supporting the four plastic filter frames. This supporting cylinder has a diameter 2 cm smaller than the impaction surface support cylinder. Underneath the filter a

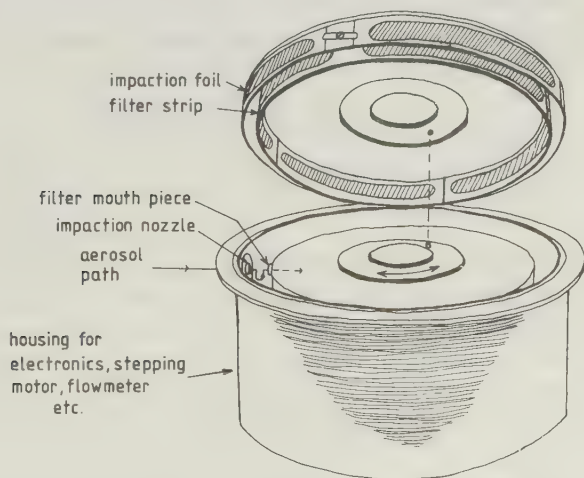


Figure 1. Schematic drawing of the sampler with the filter holder lifted.

teflon[®] mouthpiece streaks along the filter surface. This mouthpiece is connected to a pump and has an 8 mm diameter allowing a maximum flow of 5 l/min. This reduces the pressure by 270 mm Hg (relative to atmospheric pressure) for a filter with 0.3 μ m pore size. As a result of this reduction in pressure the filter is sucked close to the mouthpiece without any significant leakage. To measure the flow rate an electronic pressure gauge placed downstream of the filter is used to measure the pressure drop over a valve. The two concentric cylindrical surfaces, carrying the impaction and filter surfaces, are attached to the same circular disk. The disk is connected through a gear to a stepping motor. By turning this disk a new sampling position is obtained with fresh impaction and filtration surfaces. At the maximum flow rate of 5 l/min the maximum number of sampling points is 70.

Electronics

To allow the most possible freedom of choice of sampling strategy, a dedicated microcomputer has been developed. This makes it possible to fully control the sampler by setting, for example, the start time, the interval between samples, the sampling lengths etc. If something abnormal occurs suitable action can be taken, e.g. forced rotation of the cylinder to a new sampling area due to deviation from the preset flow rate.

The computer also stores relevant data (e.g. wind speed, wind direction, relative humidity) and is for that purpose equipped with an interface for Voltage/Frequency-converters and a non-volatile memory for data collection.

The computer is constructed around a C-MOS microprocessor, (to obtain high noise immunity and low power consumption) CDP 1805 (RCA), with a structure suitable for small controlling units with a limited need for arithmetic.

The program is written in assembly-language to obtain a compact code in a 2 k-byte Erasable Programmable Read only memory (EPROM), and was developed using an RCA Microboard Computer Development System. In order to be able to make program modifications quickly and easily, a combined editor assembler has also been developed.

The current program is an interrupt driven (50 Hz) real time system that has the following features:

1. Setting time (month, day, hour, minute)
2. Setting start time for sampling
3. Setting sampling interval and length in minutes

4. Setting the separation between sample positions (1 - 99 motor steps)
 5. Manual control of stepping motor
 6. Forced sample switching due to deviating flow rate
 7. Storage of the real time and duration for each sample in a 16 k-byte EPROM together with the values of the variables in 1, 2, 3 and 4
 8. Storage of the flow rate during sampling
- The data stored in the EPROM can be read by the developed programming unit and can easily be transferred to the same data base as the elemental concentrations from the PIXE analysis.

TESTING PROCEDURES AND RESULTS

Different kinds of laboratory experiments have been performed to test the existing prototype with respect to the demands concerning its aerodynamical properties discussed above.

Internal losses

For submicron particles the sampler was tested with an aerosol of CuSO_4 produced with the equipment shown in fig. 2. The use of a dry aerosol was justified since bounce-off effects were not considered to cause any significant changes in the results for these particle sizes. A constant output atomizer (TSI 3075) produced a polydisperse aerosol. An Electrostatic Classifier (TSI 3071) was used to

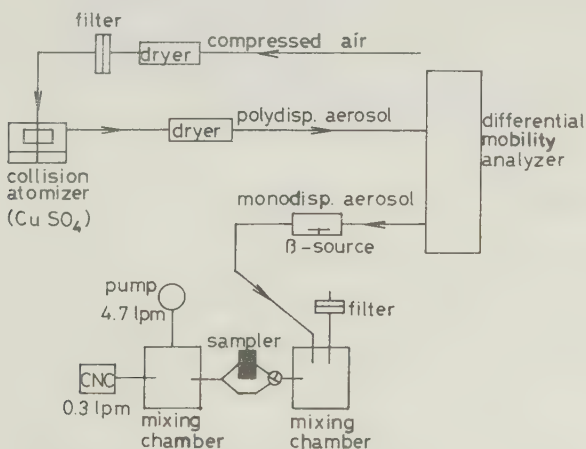


Figure 2. Experimental set-up for penetration measurements at submicron particle sizes.

select a well defined particle size and after passing a ^{85}Kr beta source the aerosol was drawn through the sampler without any filter and into a mixing chamber at a flow rate of 5 l/min. From the mixing chamber a sample of 0.3 l/min was drawn in to a Condensation Nucleus Counter (TSI 3020). The penetration was determined by comparing the concentrations with and without the sampler and the results are shown in fig. 3. During early experiments it was found that the penetration for the smaller particles varied from time to time and that the losses could exceed 25% with a non-conducting interior. Thus the experiments were performed with the interior in contact with the air stream covered with a conducting layer. The penetration was found to be between 90 and 100% throughout the whole measured particle size interval 0.02 to 0.5 μm . Since particle losses increase with decreasing particle size the losses are most probably due to diffusion losses.

The tests were performed for both the multijet and a single jet impaction nozzle to find out if submicron particles were influenced by using quite different types of impaction nozzles. The two sets of results are in good agreement and differ at most by 2-3%.

The sampling efficiency, including the filter stage, for particles larger than 0.5 μm was determined by using monodisperse methylene blue aerosols from a vibrating orifice generator (TSI 3050). The aerosol was homogenized in a mixing chamber and sampled with the sampler and a reference filter (fig. 4). To check whether the aerosol was quantitatively deposited within the area supposed to be analysed with PIXE, that is a circular area of 8 mm diameter, the impaction and filtration areas were punched out and the methylene blue was dissolved in ethyl alcohol and analysed with a spectrophotometer (Unicam SP1800, 660 nm). A summary of the results obtained for the absolute sampling efficiency of particles larger than 0.5 μm aerodynamic diameter is shown in fig. 3.

Filter efficiency

The Nuclepore filter was found to fit our sampling and analytical procedures best. The filter efficiency for two different pore diameters, 0.4 μm and 0.3 μm , was tested according to a procedure described elsewhere (19). The 0.4 μm pore diameter filter was tested at 300 and 600 mm Hg pressure drop, while the 0.3 μm filter was tested only at 300 mm Hg (a pressure drop of 600 mm Hg caused the filter to break). The flow rates obtained were 2.8 and 5 l/min for the 0.4 μm filter at pressures of 300 and 600 mm Hg respectively, and 5 l/min for the finer filter. The results are presented in fig. 5. For the same flow rate the same

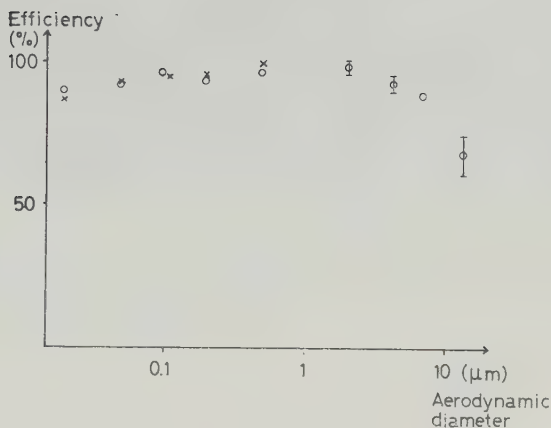


Figure 3. The efficiency for particle penetration through the sampler without filter for small particles ($D \leq 0.5 \mu\text{m}$) and the sampling efficiency for particles larger than $0.5 \mu\text{m}$. Results obtained with the multijet impaction nozzle are shown by open circles (o), and the single jet by crosses (x). Error bars show one standard deviation on the measurements made (only given $>1\%$)

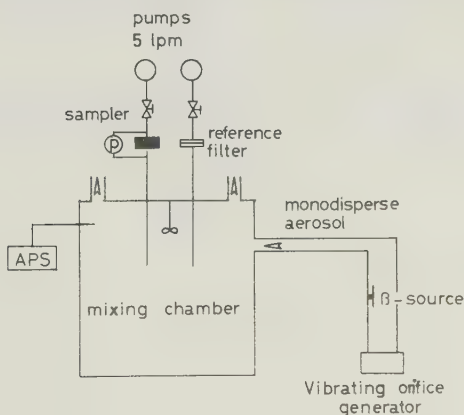


Figure 4. Experimental set-up for studying internal losses of particle sizes between 0.5 and $15 \mu\text{m}$ aerodynamic diameter.

efficiency is achieved for the two pore sizes, but when the flow rate is decreased, thereby decreasing the pressure drop, the efficiency changes by up to 10% for certain particle sizes (which can be of importance when sampling an aerosol with a significant amount of mass below $0.1 \mu\text{m}$). The $0.3 \mu\text{m}$ filter was

found to break occasionally at the pressure drop tested. However, we see that, at the high pressure drop used in this study, there were no large losses for particles above $0.05\ \mu\text{m}$. Similar, much more extensive measurements have been performed by Liu et al (20) who provide data for other pore sizes and flow rates. Particles with diameters below $0.05\ \mu\text{m}$ do not represent any significant mass in the atmospheric aerosol.

Leakage between the filter and the teflon mouthpiece was measured by using a polydisperse submicron methylene blue aerosol. The collection efficiency was measured in an experimental set-up similar to that for larger particles (see figure 4). The leakage was found to be less than 2 %.

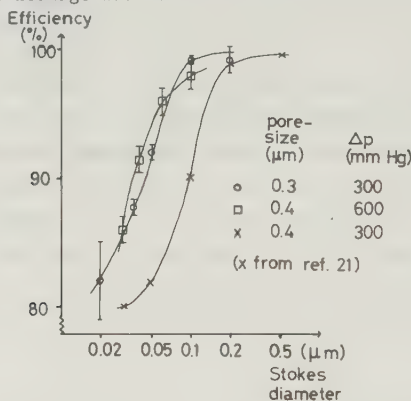


Figure 5. Collection efficiency for Nuclepore filter with pore sizes 0.3 and $0.4\ \mu\text{m}$ at differential pressures of 300 and 600 mm Hg.

Particle size fractionation

The impaction characteristics were determined by a penetration test without any filter. By comparing the penetration efficiencies with and without the impaction surface the impaction characteristics are obtained. The experimental set-up can be seen in fig. 6 consisting of a polydisperse aerosol generator, a concentric nebulizer, to generate an aerosol with particles in the size range 0.5 to $7\ \mu\text{m}$. Both dry and wet aerosols, NaCl and DOP (dioctyl phthalate) were used to illustrate losses for all kinds of aerosols. An aerodynamic particle sizer (TSI 3300) was used to detect and size classify the aerosol particles penetrating the sampler. Due to the rapidity with which impactor tests can be made in this arrangement several different impactor configurations could be tested. Besides the described 8-hole nozzle, we also tested a single orifice nozzle with a

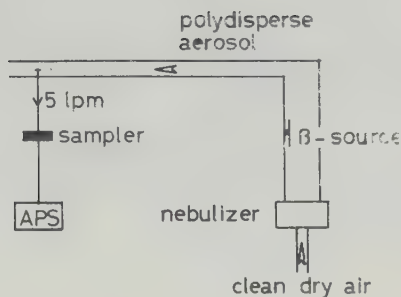


Figure 6. Experimental set-up for the characterization of the impactor in the sampler.

cut-off diameter of $2.0 \mu\text{m}$. The 8-hole nozzle was chosen due to its lower air jet velocity and larger deposition area decreasing bounce-off and giving a more evenly distributed deposition. The cut-off curves obtained with the DOP aerosol are presented in figs. 7 and 8. The internal losses given above have been disregarded. A comparison of the two experimental curves shows a less well defined cut-off for the multijet impactor. Its unusual shape is probably due to the multi-impactor design, where the channels in the nozzle have different lengths. Thus the pressure drop will be different for different holes and thereby different jet velocities will result. Fig. 7 also shows the suggested ACGIH standard for comparison (discussed earlier).

Various impaction surfaces were also investigated. The time dependence of the bounce-off was determined for Apiezon grease and low viscosity silicon oil on

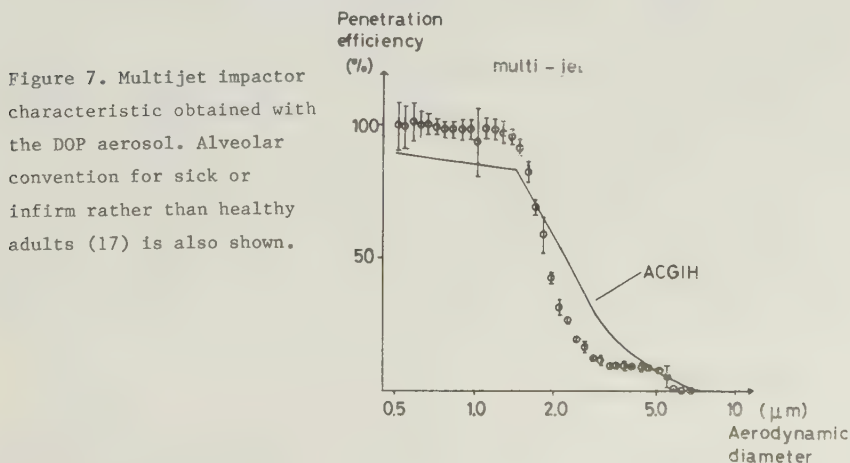
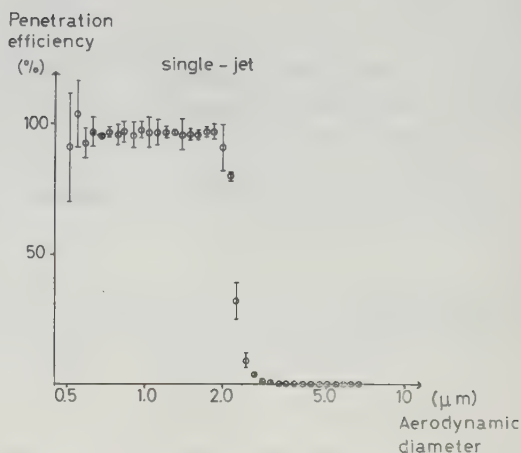


Figure 7. Multijet impactor characteristic obtained with the DOP aerosol. Alveolar convention for sick or infirm rather than healthy adults (17) is also shown.

Figure 8. Single jet impactor characteristics obtained with the DOP aerosol.



Nuclepore filters. A Kleenex paper tissue soaked with silicon oil placed under the Nuclepore filter acted as a reservoir. The test aerosol was NaCl with a mass median aerodynamic diameter of about $6\text{ }\mu\text{m}$ at a concentration of about 2 particles/ cm^3 , equivalent to a normal natural maritime aerosol. After 4 hours of exposure at a flow rate of 5 l/min the bounce-off was found to be 30% and 5 % for Apiezon grease and silicon oil, respectively.

CONCLUSIONS

An automatic two-stage aerosol sampler for stationary sampling in greatly varying outdoor environments has been constructed and tested. The sampler is constructed to give an optimized sampling and analytical system together with PIXE for atmospheric aerosol measurements. The sampler can work with varying flow rate of up to 5 l/min. The cut-off point between the two size fractions is defined by an impaction stage, which can have a cut-off between 2 and $5\text{ }\mu\text{m}$. The internal losses including wall losses, bounce-off and filtration leakage are below 15 % in the particle size range $0.05\text{--}10\text{ }\mu\text{m}$ for the maximum flow rate of 5 l/min. The number of sample positions is 70 with a flow rate of 5 l/min. A microprocessor controls the sampler and allows high flexibility in selecting the sampling program. A solid-state memory makes it possible to record sampling data both from the sampler (sampling time, flow rate) and from other meteorological instruments.

ACKNOWLEDGEMENTS

During the experimental and analytical work the discussions with Mats Bohgard and Klas Malmqvist have been most valuable and are gratefully acknowledged.

Bengt Martinsson and Erik Swietlicki have been very helpful in assisting in the laboratory experiments.

Lars-Berne Nilsson has provided excellent work in manufacturing the sampler. Skilful help with the electronics was given by Erik Karlsson.

The strong support during the whole project from Roland Akselsson has been most important.

The project was partly supported by the National (Swedish) Environment Protection Board.

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